Inorg. Chem. **2005**, *44*, 9105–9111

Inorganic Chemistry
Article

Physical Parameters and Electron-Transfer Kinetics of the Copper(II/I) Complex with the Macrocyclic Sexadentate Ligand [18]aneS_6

Gezahegn Chaka,[†] L. A. Ochrymowycz,[‡] and D. B. Rorabacher*,[†]

Departments of Chemistry, Wayne State University, Detroit, Michigan 48202, and
The University of Wisconsin—Eau Claire, Eau Claire, Wisconsin 54701

Received September 12, 2005

The electron-transfer kinetics of the complex formed by copper(II/I) with the sexadentate macrocyclic ligand 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS_6) have been measured in acetonitrile with a series of three oxidizing agents and three reducing agents. These studies have been supplemented by determinations of the redox potential and the stability constants of the Cu^{I}- and Cu^{II}([18]aneS_6) complexes in both acetonitrile and aqueous solution. The Marcus cross relationship has been applied to the cross-reaction rate constants for the six reactions studied to resolve the electron self-exchange rate constant for the $Cu^{II/I}$([18]aneS_6) complex. An average value of $k_{11} = 3 \times 10^3$ M^{-1} s^{-1} was obtained at 25 °C, $\mu = 0.10$ M in acetonitrile. This value is approximately 2 orders of magnitude smaller than the values reported previously for the corresponding Cu(II/I) complexes with the quadridentate and quinquedentate homoleptic homologues having all ethylene bridges, namely, 1,4,7,10-tetrathiacyclododecane ([12]aneS_4) and 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS_5). This significant difference in reactivity is attributed to the greater rearrangement in the geometry of the inner-coordination sphere that accompanies electron transfer in the $Cu^{II/I}$([18]aneS_6) system, wherein two Cu–S bonds are ruptured upon reduction. In contrast to other Cu(II/I) complexes with macrocyclic polythiaethers that have self-exchange rate constants within the same range, no evidence for conformationally gated electron transfer was observed, even in the case of the most rapid oxidation reaction studied.

Introduction

In previous work, we have examined the thermodynamic and kinetic properties of a variety of copper(II/I) complexes formed with macrocyclic polythiaethers.[1−6] Detailed studies on the electron-transfer kinetics of these complexes have been particularly enlightening and have demonstrated that the complexes formed with the macrocycles [12]aneS_4[7] and [15]aneS_5,[8] in which all sulfur donor atoms are linked by ethylene bridges, exhibit electron self-exchange rate constant values, k_{11}, of $\geq 10^5$ M^{-1} s^{-1}.

$$^{*}Cu^{II}L + Cu^{I}L \xrightleftharpoons{k_{11}} {}^{*}Cu^{I}L + Cu^{II}L \qquad (1)$$

These values are within the same order of magnitude as the rapidly reacting type I Cu centers in the blue copper proteins known as cupredoxins.[9] In fact, a substituted analogue of [12]aneS_4, namely, oxathiane-[12]aneS_4, has yielded a value of $k_{11} = 8 \times 10^5$ M^{-1} s^{-1} for the Cu(II/I) complex which is the largest value reported to date for any inorganic copper complex.[10] As represented schematically in Figure 1, the crystal structures of the Cu(II) complexes with [12]aneS_4,

---

* To whom correspondence should be addressed. Fax: (313) 577-8822. E-mail: dbr@chem.wayne.edu.

[†] Wayne State University.

[‡] University of Wisconsin—Eau Claire.

(1) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012−3022.

(2) Meagher, N. E.; Juntunen, K. L.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 10411−10420.

(3) Meagher, N. E.; Juntunen, K. L.; Heeg, M. J.; Salhi, C. A.; Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1994**, *33*, 670−679.

(4) Salhi, C. A.; Yu, Q.; Heeg, M. J.; Villeneuve, N. M.; Juntunen, K. L.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 6053−6064.

(5) Wijetunge, P.; Kulatilleke, C. P.; Dressel, L. T.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **2000**, *39*, 2897−2905.

(6) Yu, Q.; Salhi, C. A.; Ambundo, E. A.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 5720−5729.

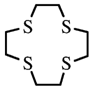
(7) Leggett, G. H.; Dunn, B. C.; Vande Linde, A. M. Q.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1993**, *32*, 5911−5918.

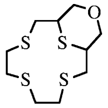
(8) Vande Linde, A. M. Q.; Juntunen, K. L.; Mols, O.; Ksebati, M. B.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1991**, *30*, 5037−5042.

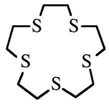
(9) Rorabacher, D. B. *Chem. Rev.* **2004**, *104*, 651−697.

10.1021/ic0515608 CCC: $30.25

oxathiane-[12]aneS_4, and [15]aneS_5 are square pyramidal[10−12] with a solvent molecule occupying the axial coordination site in the case of the 12-membered macrocyclic complexes.


[12]aneS_4

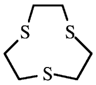

oxathiane-[12]aneS_4


[15]aneS_5

Crystal structures of the corresponding Cu(I) complexes with these three ligands reveal that one of the in-plane Cu−S bonds dissociates upon reduction to generate a distorted tetrahedral species.[10,12,13] We have attributed the redox lability of these Cu(II/I) systems to the fact that the rupture of the Cu−S bond is relatively labile and alterations in the remaining bond angles and distances are minimal in nature. The fact that no metal−solvent bonds are formed or ruptured during the electron-transfer process is also hypothesized to be a significant factor in the rapid electron-transfer kinetics as this may minimize the reorganization occurring in the surrounding solvent layer. However, the impact of the specific structural changes accompanying electron transfer is not clear.

Stanbury and co-workers[14,15] have investigated a series of interesting five-coordinate Cu(II/I) complexes with unsaturated nitrogen donor atoms that maintain all five Cu−N bonds in both oxidation states; despite the apparent constancy of their coordination geometries, the resulting self-exchange rate-constant values for these systems are significantly smaller, ranging from about 2×10^3 to 3×10^4 M^{-1} s^{-1}. Studies on systems that maintain four coordination in both oxidation states have also been reported to have k_{11} values within the same range.[16,17] The most perplexing results are those reported by the Stanbury group on two systems that also maintain four coordination in both oxidation states but yield resolved k_{11} values of only 10^{-1}−10^{-2} M^{-1} s^{-1}.[18,19]

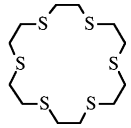
In a study related to the earlier macrocyclic polythiaether complexes cited above, we recently investigated the electron-transfer kinetic behavior of the Cu(II/I) system involving the small terdentate macrocyclic ligand [9]aneS_3.[20]

[9]aneS_3 =


This system is unique in that the Cu(II) complex involves two fully coordinated ligands (i.e., $Cu^{II}L_2$) with six donor atoms in a tetragonal arrangement,[21] while the Cu(I) oxidation state strongly favors a 1:1 complex in dilute solution with a solvent molecule or anion presumed to occupy the fourth coordination site.[20,22] Thus, electron-transfer is accompanied by the gain or loss of an entire ligand. On the basis of an estimated equilibrium constant for the addition of the second ligand to Cu^IL, we concluded that the value of the electron self-exchange rate constant, k_{11}', for the bis species was on the same order of magnitude as the values for the [12]aneS_4 and [15]aneS_5 systems, that is, $k_{11}' \geq 10^5$ M^{-1} s^{-1}.[20]

$$*Cu^{II}L_2 + Cu^IL_2 \xrightleftharpoons{k_{11}'} *Cu^IL_2 + Cu^{II}L_2 \qquad (2)$$

The study on the [9]aneS_3 complex is the only Cu(II/I) system reported to date in which the Cu(II) ion is known to be coordinated to six ligand donor atoms. However, as noted above, the overall reaction is complicated by the tendency of copper to lose one [9]aneS_3 ligand upon reduction. To circumvent this problem, we have now examined the Cu(II/I) electron-transfer kinetics for a related system in which *six* thiaether sulfur donor atoms are incorporated into a single macrocyclic ligand involving all ethylene bridges, namely, 1,4,7,10,13,16-hexathiacyclooctadecane ([18]aneS_6).

[18]aneS_6 =


Hartman and Cooper[23] have previously determined the crystal structure of both the Cu(II) and Cu(I) complexes. In the oxidized complex, all six sulfur atoms were coordinated

---

(10) Krylova, K.; Kulatilleke, C. P.; Heeg, M. J.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4322−4328.

(11) Pett, V. B.; Diaddario, L. L., Jr.; Dockal, E. R.; Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1983**, *22*, 3661−3670.

(12) Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Moy, I. W.-Y.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1985**, *107*, 2399−2404.

(13) Brooks, N. R.; Blake, A. J.; Champness, N. R.; Cooke, P. A.; Hubberstey, P.; Proserpio, D. M.; Wilson, C.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **2001**, 456−465.

(14) Goodwin, J. A.; Stanbury, D. M.; Wilson, L. J.; Eigenbrot, C. W.; Scheidt, W. R. *J. Am. Chem. Soc.* **1987**, *109*, 2979−2991.

(15) Coggin, D. K.; Gonzalez, J. A.; Kook, A. M.; Bergman, C.; Brennan, T. D.; Scheidt, W. R.; Stanbury, D. M.; Wilson, L. J. *Inorg. Chem.* **1991**, *30*, 1125−1134.

(16) Metelski, P. D.; Hinman, A. S.; Takagi, H. D.; Swaddle, T. W. *Can. J. Chem.* **1995**, *73*, 61−69.

(17) McMaster, J.; Beddoes, R. L.; Collison, D.; Eardley, D. R.; Helliwell, M.; Garner, C. D. *Chem.*−*Eur. J.* **1996**, *2*, 685−693.

(18) Xie, B.; Wilson, L. J.; Stanbury, D. M. *Inorg. Chem.* **2001**, *40*, 3606−3614.

(19) Xie, B.; Elder, T.; Wilson, L. J.; Stanbury, D. M. *Inorg. Chem.* **1999**, *38*, 12−19.

(20) Kandegedara, A.; Krylova, K.; Nelson, T. J.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Chem. Soc., Dalton Trans.* **2002**, 792−801.

(21) Glass, R. S.; Steffen, L. K.; Swanson, D. D.; Wilson, G. S.; de Gelder, R.; de Graaff, R. A. G.; Reedijk, J. *Inorg. Chim. Acta* **1993**, *207*, 241−252. (b) Setzer, W. N.; Ogle, C. A.; Wilson, G. S.; Glass, R. S. *Inorg. Chem.* **1983**, *22*, 266−271.

(22) Wilson and co-workers have obtained a crystal structure of Cu^I([9]aneS_3)$_2$ in which one ligand was coordinated through all three sulfur donor atoms while the second ligand molecule was coordinated through only one Cu−S bond: Sanaullah; Kano, K.; Glass, R. S.; Wilson, G. S. *J. Am. Chem. Soc.* **1993**, *115*, 592−600. (The same basic structure has been observed in related ternary complexes of the type Cu^I([9]aneS_3)(Z) where Z is a second ligand species coordinated to Cu(I) through a single thiaether sulfur donor atom: Sanaullah; Hungerbühler, H.; Schöneich, C.; Morton, M.; Vander Velde, D. G.; Wilson, G. S.; Asmus, K.-D.; Glass, R. S. *J. Am. Chem. Soc.* **1997**, *119*, 2134−2145.) This led them to assume that the reduced complex exists as Cu^IL_2 is solution. However, electrochemical and electron-transfer kinetic studies show that the reduced complex involves only a single coordinated [9]aneS_3 ligand in solution, see ref 20.

(23) Hartman, J. R.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1202−1208.

to the copper atom. Upon reduction, two adjacent Cu−S bonds ruptured. The structural similarity of this system to the bis complex, Cu$^{II/I}$([9]aneS$_3$)$_2$, suggested that the Cu$^{II/I}$([18]aneS$_6$) system might exchange electrons rapidly. Therefore, a thorough kinetic study of the latter system appeared to be warranted. Accordingly, the electron-transfer kinetics of this system reacting with a series of counter oxidants and reductants have been determined in acetonitrile to ensure sufficient ligand solubility. Since no thermodynamic measurements have previously been reported for the Cu$^{II/I}$([18]aneS$_6$) system, we have also determined the Cu$^{II/I}$L potentials in both acetonitrile and water as well as the stability constants of the oxidized and reduced complexes.

Experimental Section

Reagents. An initial sample of [18]aneS$_6$ was prepared by a previously published method.[24] Additional amounts of this compound were later obtained from Aldrich Chemicals and used without further purification since the NMR spectrum showed no evidence of significant contaminants. The counter reagent Ni^{II}([9]aneN$_3$)$_2$(ClO$_4$)$_2$ was prepared by the method of McAuley et al.[25] ***Caution!*** *All metal perchlorate salts are potentially explosive and should be handled with extreme care. These compounds should be prepared in small quantities and should never be dried.* All other counter reagents used in this work, as well as the copper(II) and copper(I) perchlorate salts in acetonitrile, were prepared by literature methods, as previously reported.[3,26] Since sodium perchlorate appeared to accelerate the degradation of the copper complex in acetonitrile, the ionic strength in the latter solvent was controlled with tetra-*n*-butylammonium hexafluorophosphate (Bu$_4$NPF$_6$), which was obtained from Aldrich and used without further purification. For the studies in aqueous solution, sodium nitrate and nitric acid were used for the same purpose. The acetonitrile solvent was HPLC grade from Fisher Scientific. Previous measurements have shown that this solvent contains very little water,[26] and additional water in small amounts had no effect on the electron-transfer kinetics. For the aqueous measurements, distilled-deionized water of conductivity grade was used.

Electrochemical Measurements. Cyclic voltammograms of Cu$^{II/I}$L were obtained using a BAS 100 electrochemical work station (Bioanalytical Systems, Lafayette, IN) operated at ambient temperature. A three-electrode electrochemical cell was used consisting of a 3 mm glassy carbon disk working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl (3 M NaCl) reference electrode (from Bioanalytical Systems); the last electrode has a measured aqueous potential of 0.226 V vs SHE (as contrasted to the supplier's published potential value of 0.208 V).[27]

To avoid ambiguity in the potentials reported, all aqueous potentials were measured using ferroin in 0.05 M NaCl as an external standard. The potential of ferroin has been accurately determined as $E^f = 1.117$ V vs SHE,[28] and on the basis of this reference potential, the aqueous potentials of all other species were corrected to SHE. Potentials in acetonitrile were referenced to ferrocene as either an internal or external standard as recommended by IUPAC.[29] All formal potentials were taken as the half-wave potentials obtained from slow-scan voltammograms ($\upsilon = 10-100$ mV s^{-1}). The same instrumentation was utilized for the determination of the Cu^{I}L stability constant by pulsed square-wave voltammetry (vide infra).

Table 1. Physical Parameters for Cu$^{II/I}$([18]aneS$_6$) in Acetonitrile and in Aqueous Solution at 25 °C, $\mu = 0.10$ M[a]

	acetonitrile	aqueous
E^f (V)	0.382[b]	0.789[c,d]
λ_{max} (nm) (Cu^{II}L)	442	438
$\epsilon_{Cu^{II}L}$ (M^{-1} cm^{-1}) (Cu^{II}L)	7.6×10^3	5×10^3
$K_{Cu^{I}L}$ (M^{-1})	1.15×10^4	$\sim 6 \times 10^{14}$
$K_{Cu^{II}L}$ (M^{-1})	1.2×10^8	$\sim 5 \times 10^3$

[a] Ionic strength maintained with Bu$_4$NPF$_6$ in acetonitrile and with NaNO$_3$/HNO$_3$ in aqueous solution. [b] Relative to ferrocene as determined for a solution containing 0.16 mM Cu(II) and 0.91 mM [18]aneS$_6$. [c] Relative to SHE. [d] Hartman and Cooper report a potential value of +0.72 V vs a saturated calomel electrode in nitromethane (ref 23).

Kinetic Measurements. All kinetic measurements were made using a Durrum D-110 stopped-flow spectrophotometer interfaced to a microcomputer with a Metrabyte 12 bit A/D board. The instrument used was equipped with a modified flow system, designed and built by Tritech Scientific Ltd. of Winnipeg, Manitoba, Canada. This flow system contained all Teflon gaskets, thereby avoiding the leakage problems inherent when using acetonitrile in the original rubber gasket system. The temperature of all solutions was maintained at 25.0 ± 0.2 °C using a circulating water bath. The kinetic data were analyzed using software developed in house. Absorbance data for the stability constant determinations on the Cu(II) complexes were obtained using a Cary 17D double-beam recording spectrophotometer equipped with a thermostated cell compartment.

Results

Redox Potentials. The Cu$^{II/I}$L potential for [18]aneS$_6$ was determined in both acetonitrile and water by means of slow-scan cyclic voltammetry ($\upsilon \geq 10$ mV s^{-1}). The voltammograms were reversible with peak separations of 62 and 58 mV in acetonitrile and water, respectively. The resultant values are included in Table 1. The use of Bu$_4$NPF$_6$ for ionic strength control was observed to result in slightly higher potential values; therefore, the formal potentials of all counter reagents were redetermined in this salt. These latter values are listed in Table 2.

Stability Constant Determination. The Cu^{II}L complex is relatively weak in aqueous solution. Therefore, the magnitude of the stability constant and the molar absorptivity of the complex were determined simultaneously using the method of McConnell and Davidson,[30] as previously described.[31] Because of solubility limitations in aqueous solution, the [18]aneS$_6$ system was primarily studied in

---

(24) Wolf, R.; Hartman, J. R.; Ochrymowycz, L. A.; Cooper, S. R. *Inorg. Synth.* **1989**, *25*, 122−126.

(25) McAuley, A.; Norman, P. R.; Olubuyide, O. *J. Chem. Soc., Dalton Trans.* **1984**, 1501−1505.

(26) Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 1954−1956

(27) Ambundo, E. A.; Deydier, M.-V.; Grall, A. J.; Aguera-Vega, N.; Dressel, L. T.; Cooper, T. H.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1999**, *38*, 4233−4242; see footnote 66.

(28) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1980**, *101*, 1131−1132.

(29) Gritzner, G.; Kuta, J. *Pure Appl. Chem.* **1984**, *56*, 461−466.

(30) McConnell, H.; Davidson, N. *J. Am. Chem. Soc.* **1950**, *72*, 3164−3167. (b) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703−2707.

(31) Aronne, L.; Dunn, B. C.; Vyvyan, J. R.; Souvignier, C. W.; Mayer, M. J.; Howard, T. A.; Salhi, C. A.; Goldie, S. N.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1995**, *34*, 357−369.

Table 2. Physical Properties of Counter Reagents in Acetonitrile at 25 °C, $\mu = 0.10$ M (Bu_4NPF_6)

reagents[a]	E^f (V vs Fc)[b]	k_{22} ($\times 10^{-5}$ M^{-1} s^{-1})	r ($\times 10^8$ cm)	λ_{max} (nm)	ϵ ($\times 10^{-3}$ M^{-1} cm^{-1})
reductants					
$Ru^{II}(NH_3)_4phen$	0.155	5.5[c]	4.4[d]	471[e]	7.57[e]
$Ru^{II}(NH_3)_4bpy$	0.152	5.5[f]	4.4[d]	522[g]	3.31[g]
$Ru^{II}(NH_3)_5isn$	0.053	4.7[f]	3.8[g]	478[h]	11.9[h]
oxidants					
$Ni^{III}([14]aneN_4)$	0.601	0.033[i]	3.6[i]	308[j]	11[j]
$Ni^{III}([9]aneN_3)_2$	0.587	0.021[k]	4.5[k]	312[k]	11.1[k]
$Fe^{III}(bpy)_3$	0.673	37[l]	6.0[d]	522[m]	8.65[m]

[a] For ligand abbreviations, see text. [b] This work; the effective radius (r) for $Cu^{II/I}([18]aneS_6)$ was assumed to be equal to the values used previously for $Cu^{II/I}([14]aneS_4)$ (ref 1). [c] Assumed to be equal to the corresponding bipyridyl complex. [d] Ref 1. [e] Stanbury, D. M.; Haas, O.; Taube, H. *Inorg. Chem.* **1980**, *19*, 518−524. [f] Ref 26. [g] Brown, G. M.; Sutin, N. *J. Am. Chem. Soc.* **1979**, *101*, 883−892. [h] Shepard, R.; Taube, H. *Inorg. Chem.* **1973**, *12*, 1392−1401. [i] Fairbank, M. G.; Norman, P. R.; McAuley, A. *Inorg. Chem.* **1985**, *24*, 2639−2644. [j] Zeigerson, E.; Ginzburg, G.; Schwartz, N.; Luz, Z.; Meyerstein, D. *J. Chem. Soc., Chem. Commun.* **1979**, *82*, 241−243. [k] Ref 20. [l] Chan, M. S.; Wahl, A. C. *J. Phys. Chem.* **1978**, *82*, 2542−2549. [m] Brandt, W. W.; Smith, G. F. *Anal. Chem.* **1949**, *21*, 1313−1319.

acetonitrile. The strong affinity of Cu(I) for acetonitrile resulted in a relatively weak Cu^IL complex in the latter solvent. To verify the magnitude of the Cu^IL stability constant in acetonitrile, we utilized the Osteryoung square-wave voltammetric approach,[32] as previously described.[31] The value of the $Cu^I([18]aneS_6)^+$ stability constant in acetonitrile was found to be 1.15×10^4 M^{-1}. The stability constant for the corresponding $Cu^{II}L$ complex was estimated from the Cu^IL stability constant using the Nernst equation in the form

$$E^f = E^{0}_{solv}{}' - \frac{2.303RT}{n\mathscr{F}} \log \frac{K_{Cu^{II}L}}{K_{Cu^{I}L}} \qquad (3)$$

where $E^{0}_{solv}{}'$ represents the potential for the solvated Cu(II/I) redox couple which was determined to be 0.619 V (vs ferrocene) in acetonitrile in the presence of 0.10 M Bu_4NPF_6. Similarly, eq 3 was used to calculate the value of K_{Cu^IL} in aqueous solution from the experimental aqueous $K_{Cu^{II}L}$ value using a previously calculated value of $E^{0}_{solv}{}' = 0.13$ V (vs SHE).[31] The resultant values for the stability constants of both the oxidized and reduced complexes in both solvents are listed in Table 1.

The relatively small K_{Cu^IL} value in acetonitrile compares favorably to the value of 1.6×10^4 M^{-1} found previously for $Cu^I([14]aneS_4)^+$ in this solvent.[31] This implies that, when stoichiometric quantities of Cu(I) and ligand are present in dilute solution, much of the reduced complex is dissociated. To compensate for this, studies on the oxidation kinetics of $Cu^I([18]aneS_6)^+$ were conducted on solutions which contained >10 mM total ligand concentration to ensure that nearly all Cu(I) would be present in the complexed form.

Since the stability constant for $Cu^{II}([18]aneS_6)^{2+}$ in acetonitrile is large, this complex is essentially fully formed when stoichiometric quantities of Cu(II) and the ligand are present in solution. Therefore, the molar absorptivity value for $Cu^{II}([18]aneS_6)^{2+}$ in acetonitrile was determined directly from mole-ratio plots using the visible wavelength of maximum absorbance. The resulting value is included in Table 1.

Electron-Transfer Kinetics. The electron-transfer kinetics for the $Cu^{II/I}([18]aneS_6)$ redox couple were studied in acetonitrile using cross reactions involving a series of counter reagents as represented by the reaction

$$Cu^{II}L + A_{Red} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Cu^{I}L + A_{Ox} \qquad (4)$$

Three ruthenium complexes were selected as reducing agents (A_{Red}) including $Ru^{II}(NH_3)_4bpy^{2+}$, $Ru^{II}(NH_3)_4phen^{2+}$, and $Ru^{II}(NH_3)_5isn^{2+}$ (bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, isn = isonicotinamide). For oxidizing agents (A_{Ox}), we used $Ni^{III}([14]aneN_4)^{3+}$, $Ni^{III}([9]aneN_3)_2{}^{3+}$, and $Fe^{III}(bpy)_3{}^{3+}$ ($[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane = cyclam; $[9]aneN_3$ = 1,4,7-triazacyclononane = tacn). The properties for each of these reagents in acetonitrile are listed in Table 2. As noted above, a large excess of ligand was utilized for all Cu^IL oxidation studies to force the complex to be fully formed.[33]

The reactions involving the reduction of $Cu^{II}L$ with all three reducing reagents and the oxidation of Cu^IL with $Fe^{III}(bpy)_3{}^{3+}$ were all very fast having second-order rate constants in the range of 10^6−10^8 M^{-1} s^{-1}. To observe these reactions while maintaining sufficient sensitivity, all four reactions were studied under second-order conditions in which the last segment of the reaction was followed.[34] The other two reactions involving the oxidation of Cu^IL were studied under pseudo-first-order conditions in which the Ni(III) counter reagent was maintained in large excess and varied over a 7- to 8-fold range. The pseudo-first-order rate constant values were then plotted against the concentration of the Ni(III) reagent, and the second-order rate constant, k_{21}, was determined from the slope. The resolved second-order rate constants for all six reactions are listed in Table 3. (Tables of experimental rate constant data are provided in the Supporting Information.)

Discussion

Redox Potential and Complex Stabilities. In their initial studies on the $Cu^{II/I}([18]aneS_6)$ system in nitromethane,

---

(32) Christie, J. H.; Turner, J. A.; Osteryoung, R. A. *Anal. Chem.* **1977**, *49*, 1899−1903.

(33) The use of excess ligand, as well as the dilute solutions used in the current work, had the added advantage of preventing the formation of the binuclear $Cu_2([18]aneS_6)$ species obtained by Schröder and co-workers: Blake, A. J.; Gould, R. O.; Holder, A. J.; Lavery, A. J.; Schröder, M. *Polyhedron* **1990**, *9*, 2919−2924.

(34) Dunn, B. C.; Meagher, N. E.; Rorabacher, D. B. *J. Phys. Chem.* **1996**, *100*, 16925−26933.

Table 3. Cross-Reaction Rate Constants for Reactions Involving Cu$^{II/I}$([18]aneS$_6$) and Resolved Electron Self-Exchange Rate Constants in Acetonitrile at 25 °C, $\mu = 0.10$ (Bu$_4$NPF$_6$)

counter reagent	k_{12} or k_{21} ($\times 10^{-6}$ M^{-1} s^{-1})	log k_{11} (M^{-1} s^{-1})
reductions		
Ru^{II}(NH$_3$)$_4$phen	5.2(7)	3.98
Ru^{II}(NH$_3$)$_4$bpy	2.1(5)	3.11
Ru^{II}(NH$_3$)$_5$isn	61(12)[a]	4.38[a]
oxidations		
Ni^{III}([14]aneN$_4$)	0.32(1)	3.49
Ni^{III}([9]aneN$_3$)$_2$	0.057(4)	2.58[b]
Fe^{III}(bpy)$_3$	18(8)	3.59

[a] The reduction reaction with Ru^{II}(NH$_3$)$_5$isn is of limited accuracy because of the extremely fast reaction rate. [b] The smaller log k_{11} value for the oxidation with Ni^{III}([9]aneN$_3$)$_2$ may reflect an erroneous self-exchange rate constant for the counter reagent (see text).

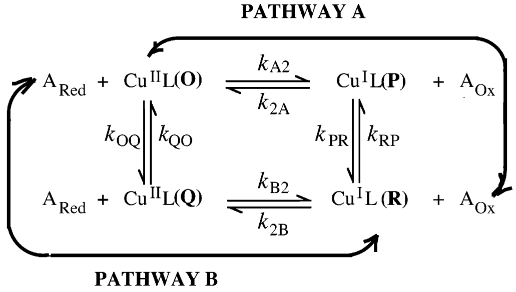
Hartman and Cooper[23] commented on the very high redox potential for this complex and suggested that this was the result of the π acidity of the sulfur donor atoms. A similar high potential is observed from our measurements in aqueous solution (Table 1). As we have reported previously,[9,27] the potentials of a wide variety of copper complexes involving amine and imine nitrogen donor atoms and thioether sulfurs in aqueous solution show that the Cu(II/I) redox potentials are primarily a function of the stability of the Cu(II) complex. However, it is interesting to note that, despite the fact that the aqueous stability constant for the Cu^{II}([18]aneS$_6$)$^{2+}$ complex ($\sim 5 \times 10^3$) appears to be only slightly smaller than that for Cu^{II}([14]aneS$_4$)$^{2+}$ ($K_{\mathrm{Cu^{II}L}} = 2.2 \times 10^4$),[35] the potential for Cu$^{II/I}$([18]aneS$_6$) is about 0.2 V higher than that for Cu$^{II/I}$([14]aneS$_4$) (0.78 V vs 0.59 V).[36] This is reflected in the fact that the aqueous stability constant for Cu^{I}([18]aneS$_6$)$^+$ (6×10^{14}) is 10^3 larger than that for Cu^{I}([14]aneS$_4$)$^+$ ($\sim 6 \times 10^{11}$), as well as for the complexes with the related 12-, 13-, 15-, and 16-membered S$_4$ macrocycles ($10^{10}-10^{12}$).[36] Thus, Hartman and Cooper were incorrect in concluding that the geometry of the [18]aneS$_6$ ligand *disfavors* the Cu(I) complex. Clearly, the larger 18-membered macrocycle has more flexibility to accommodate the tetrahedral geometry commonly encountered for Cu(I) complexes than do the smaller macrocycles.

Electron-Transfer Kinetics. For each reaction studied, the k_{11} value for the Cu$^{II/I}$L redox couple was calculated from the overall cross-reaction rate constant, k_{12} or k_{21}, using the Marcus cross relationship[37] in the form[10]

$$k_{11} = \frac{k_{12}^{\,2}}{k_{22}K_{12}f_{12}W_{12}^{\,2}} \qquad (5)$$

In eq 5, k_{22} represents the electron self-exchange rate constant for the counter reagent used (Table 2); K_{12} represents the theoretical equilibrium constant for reaction 4, on the basis of the potential values for the reactants as listed in Tables 1 and 2; f_{12} represents a nonlinear correction term;[1,37] and W_{12} represents an electrostatic work term correction.[1,37] The logarithmic values of k_{11} determined in this manner from each of the six reactions are included in Table 3.

Scheme 1



For a number of Cu(II/I) systems studied previously in our laboratory, the k_{11} values obtained for very fast oxidation reactions were often significantly smaller than the k_{11} values obtained for reduction.[1−7,38] This behavior has been attributed to a dual-pathway square-scheme mechanism (Scheme 1)[2,3,9] in which the major conformational change (vertical reactions) and the electron-transfer step (horizontal reactions) occur sequentially rather than concertedly.

The more favorable pathway will generally be dictated by the relative stability of the two metastable intermediate species, designated as P and Q, since the two electron-transfer steps are presumed to exhibit similar rate constants.[6] However, when the reaction is carried out in the direction in which *conformational change precedes electron transfer* by the more favored pathway, the conformational change itself can become rate limiting, and, ultimately, the alternate pathway can become dominant.[9] In the current study, the significant change in geometry upon changing the oxidation state in Cu$^{II/I}$([18]aneS$_6$) suggests that a similar dual-pathway mechanism should occur. However, the same k_{11} value was obtained for all oxidation and reduction reactions. If a change in pathway were induced, it should occur only in one direction and would be manifested by the appearance of a smaller k_{11} value for the *fastest* cross reactions. By contrast, the fastest reaction in the current study, namely, the reduction of Cu^{II}([18]aneS$_6$)$^{2+}$ with Ru^{II}(NH$_3$)$_5$isn^{2+}, yielded the largest k_{11} value. The latter k_{11} value is acknowledged to be of limited accuracy, however, since the cross-reaction rate constant from which it was derived is nearly 10^8 M^{-1} s^{-1} which represents our upper detection limit.[34] It is also pertinent that the oxidation reaction with Fe^{III}(bpy)$_3$$^{3+}$, which has a second-order rate constant exceeding 10^7 M^{-1} s^{-1}, yields a k_{11} value that is essentially the average of the values for the other five reactions. Moreover, the smallest k_{11} value was generated from the *slowest* reaction, that is, the one involving Ni^{III}([9]aneN$_3$)$_2$$^{3+}$ as the counter oxidant. We suspect that the self-exchange rate constant used for the Ni^{III}([9]aneN$_3$)$_2$$^{3+}$ reagent may be too large since this would yield a small k_{11} value using eq 5. This assumption is consistent with the fact that we have noted some tendency for a previous reaction with this reagent to generate a smaller k_{11} value.[20]

---

(35) Sokol, L. S. W. L.; Ochrymowycz, L. A.; Rorabacher, D. B. **1981**, *20*, 3189−3195.

(36) Bernardo, M. M.; Schroeder, R. R.; Rorabacher, D. B. *Inorg. Chem.* **1991**, *30*, 1241−1247.

(37) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265−322.

(38) Dunn, B. C.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1997**, *36*, 3253−3257.

Table 4. Geometric Changes Accompanying Reduction of Cu(II) to Cu(I) in Macrocyclic Polythiaether Complexes Containing All Ethylene Bridges

	Cu−S1	Cu−S2	Cu−X3[a]	Cu−S4[b]	Cu−S5[b]	Cu−S6
			axial			axial
$Cu^{II}([12]aneS_4)$[c]	2.34	2.30	2.11 (O)	2.37	2.32	−
$Cu^{I}([12]aneS_4)$[d]	2.33	2.47	2.27 (Cl)	2.33	−	−
Cu^{II}(oxathiane$[12]aneS_4$)[e]	2.33	2.31	2.09 (O)	2.32	2.36	−
Cu^{I}(oxathiane$[12]aneS_4$)[e]	2.37	2.37	1.97 (N)	2.36	−	−
$Cu^{II}([15]aneS_5)$[f]	2.32	2.33	2.40	2.34	2.29	−
$Cu^{I}([15]aneS_5)_5$[f]	2.24	2.34	2.32	2.25	−	−
$Cu^{II}([18]aneS_6)$[g]	2.402	2.323	2.635	2.402	2.323	2.635
$Cu^{I}([18]aneS_6)$[g]	2.358	2.245	2.360	2.253	−	−

	S1−Cu−S2	S2−Cu−X3[h]	X3−Cu−S4[h]	S4−Cu−S[i]	S5−Cu−S6[i]	S6−Cu−S1	S1−Cu−S3[j]
			axial			axial	trans
$Cu^{II}([12]aneS_4)$[c]	94.1	86.5	152.6 (O)	81.4	85.8	−	156.7
$Cu^{I}([12]aneS_4)$[d]	89.3	86.0	124.6 (Cl)	−	−	−	125.1
Cu^{II}(oxathiane$[12]aneS_4$)[e]	87.0	88.7	107.8 (O)	86.6	86.6	−	140.4
Cu^{I}(oxathiane$[12]aneS_4$)[e]	91.3	89.2	127.4 (N)	−	−	−	124.7
$Cu^{II}([15]aneS_5)$ [f]	88.5	91.9	90.8	88.7	84.6	−	164.4
$Cu^{I}([15]aneS_5)$ [f]	95.5	93.5	90.8	−	−	−	135.6
$Cu^{II}([18]aneS_6)$[g]	89.5	85.7	87.6	89.5	85.7	87.6	180.0
$Cu^{I}([18]aneS_6)$[g]	94.4	91.2	95.3	−	−	−	113.9

[a] For the 12-membered macrocycles, the Cu−X3 distance represents the bond between the copper ion and the axially coordinated H_2O, Cl^-, or CH_3CN as indicated; in the larger macrcocycles, X3 represents the third sulfur atom. [b] For the 12-membered macrocycles, S4 and S5 are actually the third and fourth sulfur donor atoms; for these reduced complexes, the fourth sulfur is not coordinated (see Figure 1). [c] Ref 11. [d] Ref 13. [e] Ref 10. [f] Ref 12. [g] Ref 23. [h] For the 12-membered macrocycles, S2−Cu−X3 represents the angle between a planar coordinated sulfur atom and the apical H_2O, Cl, or CH_3CN ligand, while the X3−Cu−S4 angle represents the angle between the second and third sulfurs in the plane. [i] For the 12-membered macrocycles, the S4−Cu−S5 angle actually involves the third and fourth sulfur donor atoms in the ring, and the S5−Cu−S6 bond angle represents the angle involving the fourth and first sulfur donor atoms; for the corresponding reduced complexes, the fourth sulfur is no longer coordinated. For the 15-membered macrocycle, the S5−Cu−S6 angle is actually the S−Cu−S angle involving the fifth and first sulfurs in the macrocycle. [j] The S1−Cu−S3 angle represents the angle formed by donor atoms on opposite sides of the "plane" (i.e., trans within the macrocyclic plane).

On the basis of the foregoing analysis of our data, we conclude that the conformational change in $Cu^{II/I}([18]aneS_6)$ for the preferred reaction pathway is sufficiently rapid that it never became rate-limiting. As a result, it is not possible to determine which pathway (Pathway A or B in Scheme 1) is preferred for electron-transfer reactions involving the $Cu^{II/I}([18]aneS_6)$ system. However, by analogy to related systems with unconstrained macrocyclic polythiaethers,[2−7] it is presumed that all k_{11} values obtained in this study represent Pathway A.

Structural Changes. The median k_{11} value from all six reactions is 3×10^3 M^{-1} s^{-1}. This is approximately 2 orders of magnitude smaller than the values obtained previously for $Cu^{II/I}$(oxathiane-$[12]aneS_4$) (8×10^5 M^{-1} s^{-1})[10] and for $Cu^{II/I}([15]aneS_5)$ (2×10^5 M^{-1} s^{-1}).[8] As noted in the Introduction, the reduction of the latter two systems is accompanied by the rupture of a single Cu−S bond, and alterations in the remaining bond angles and distances are relatively small as shown by the comparative crystal structural data in Table 4. In the $Cu^{II}([18]aneS_6)^{2+}$ complex, the copper ion is coordinated to all six donor atoms with each set of three adjacent sulfurs surrounding an octahedral face to form the meso isomer.[23,39] Reduction is accompanied

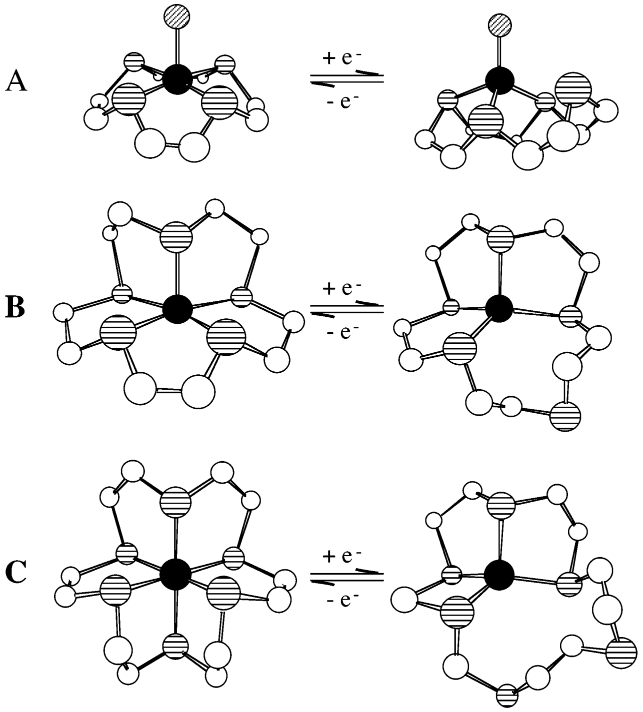


Figure 1. Structural changes accompanying electron transfer as indicated by crystal structures for Cu(II/) complexes with macrocyclic tetra-, penta-, and hexa-thiaethers containing all ethylene bridges: (A) $Cu^{II/I}([12]aneS_4)$-(H_2O),[11,13] (B) $Cu^{II/I}([15]aneS_5)$,[12] and (C) $Cu^{II/I}([18]aneS_6)$.[23] In each schematic, the solid circle represents the copper atom, the horizontally striped circles are sulfur atoms, the diagonally striped atoms are oxygen atoms (from water), and the open circles are carbons. Hydrogen atoms have been omitted for clarity. The numbering of the sulfur atoms corresponding to the bond distances and angles listed in Table 4 commences with the sulfur in the left foregound as S1 and proceeds clockwise around the macrocyclic ring.

---

(39) A *racemic* isomer is also possible in which three adjacent S donor atoms are aligned along a single octahedral edge (see ref 23). However, like Cu(II), the crystal structures reported for the $[18]aneS_6$ complexes formed with (a) Ag(I), (b) Co(II), (c) Co(III), and (d) Tl(I) are all in the meso arrangement, suggesting that this is the more stable isomer: (a) Blake, A. J.; Gould, R. O.; Holder, A. J.; Hyde, T. I.; Schröder, M. *Polyhedron*, **1989**, *8*, 513−518. (b) Hartmann, J. R.; Hintsa, E. J.; Cooper, S. R. *J. Am. Chem. Soc.* **1986**, *108*, 1208−1214. (c) Grant, G. J.; Shoup, S. S.; Hadden, C. E.; VanDerveer, D. G. *Inorg. Chim. Acta* **1998**, *274*, 192−200. (d) Blake, A. J.; Reid, G.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2987−2992.

by the rupture of two *adjacent* Cu−S bonds (Figure 1).[23,40,41] Of the four Cu−S bonds that are retained, at least one must represent an initial axial bond that has shortened by approximately 0.28 Å, and the other three Cu−S bonds have shortened to a greater extent, on average, than is the case with the smaller macrocyclic systems. It is also noteworthy that the remaining S−Cu−S bond angles have changed slightly more for Cu$^{II/I}$([18]aneS$_6$) than is the case for Cu$^{II/I}$([15]aneS$_5$),[12] which also retains four Cu−S bonds upon reduction. Thus, the significant decrease in the k_{11} value for the [18]aneS$_6$ system relative to those of [12]aneS$_4$, oxathiane-[12]aneS$_4$, and [15]aneS$_5$ is consistent with the greater changes in the copper coordination geometry.

The observation that the Cu$^{II/I}$([18]aneS$_6$) k_{11} value is also about 2 orders of magnitude smaller than the value estimated for the bis complex with [9]aneS$_3$[20] might appear somewhat surprising since two Cu−S bonds must be ruptured in both cases. However, the smaller macrocycle is considerably more rigid, thereby limiting the change in S−Cu−S bond angles accompanying the electron-transfer step. It is particularly interesting, although possibly somewhat fortuitous, that the resolved k_{11} value for the Cu$^{II/I}$([18]aneS$_6$) system is similar to that obtained for Cu$^{II/I}$([14]aneS$_4$) reacting by its favored reaction pathway (viz., 8×10^3 M^{-1} s^{-1}).[2] In the latter system, two weak Cu−OH$_2$ bonds are ruptured upon reduction and similar significant changes in bond angles occur.[42,43]

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-0211696.

Supporting Information Available: Tables of the kinetic data for the Cu(II/I) electron-transfer cross reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0515608

---

(40) The same crystal structure has been observed for Au^{I}([18]aneS$_6$): Blake, A. J.; Taylor, A.; Schröder, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1097−1098.

(41) Polymeric Cu(I) complexes have also been observed in the presence of chloride ion: (a) Rogers, R. D.; Nunez, L. *J. Coord. Chem.* **1990**, *21*, 111−118. (b) Blake, A. J.; Lippolis, V.; Parsons, S.; Schröder, M. *Acta Crystallogr.* **2001**, *C57*, 36−37.

(42) Glick, M. D.; Gavel, D. P.; Diaddario, L. L.; Rorabacher, D. B. *Inorg. Chem.* **1976**, *15*, 1190−1193.

(43) Dockal, E. R.; Diaddario, L. L.; Glick, M. D.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1977**, *99*, 4530−4532.