of the Pt(II) center to the electronic properties of the coordinated and entering ligands.

For the exchange reactions listed in Table II, there is no obvious correlation between the entropies and volumes of activation. The magnitudes of the activation volumes for the solvent exchange on Pd(II) are always smaller than for the corresponding exchange on Pt(II). With exception of the thioether complexes, the activation volumes reported so far are very small, generally not exceeding 20% of the molar volume of the entering ligand. This might indicate either that the associative character is weak or that additional effects such as bond stretching in the transition state or solvational changes decrease the volumes that should be expected for associative reactions. Exchange of thioethers display much larger activation volumes. However, it is still an open question whether this is due to changes in solvation, to an increasingly associative behavior expected for such sulfur-bonding ligands, or to a combination of both.

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Supplementary Material Available: Second-order rate constants and chemical shifts for the ligand exchange on ML_n^{2+} as a function of temperature (Tables SI–SIII) and pressure (Tables SIV–SVI) and observed rate constants and longitudinal relaxation rates obtained from the magnetization transfer experiments (Tables SVII and SVIII) (5 pages). Ordering information is given on any current masthead page.

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Direct Determination of the Self-Exchange Electron-Transfer Rate Constant for a Copper(II/I) Macrocyclic Pentathiaether Complex

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The value of the self-exchange electron-transfer rate constant for the macrocyclic pentathiaether complex $Cu^{II/I}([15]aneS_5)$ has been determined using ^1H NMR line-broadening measurements, both in D_2O and in 80% CD_3OD–20% D_2O (w/w). In the pure D_2O solvent studied over a range of 3 pD units and with varying amounts of excess $Cu^{2+}(aq)$ ion present, the best estimate of the 25 °C self-exchange rate constant is $k_{11} = 2 \times 10^5\ M^{-1}\,s^{-1}$ with activation parameters of $\Delta H^* = 14.0 \pm 4.0$ kJ mol^{-1} and $\Delta S^* = -103 \pm 11$ J $mol^{-1}\,K^{-1}$. On the basis of a single determination in 80% CD_3OD–20% D_2O, the corresponding values are $k_{11} = 0.8 \times 10^5\ M^{-1}\,s^{-1}$ (25 °C), $\Delta H^* = 19.6 \pm 1.1$ kJ mol^{-1}, and $\Delta S^* = -77$ [illegible] 4 J $mol^{-1}\,K^{-1}$. The 25 °C k_{11} value in D_2O is in virtual agreement with the corresponding calculated self-exchange rate constant value obtained by application of the Marcus cross relationship to the experimental rate constants previously reported for the *reduction* of $Cu^{II}([15]aneS_5)$ with ruthenium(II) and cobalt(II) complexes ($k_{11(Red)} = 3 \times 10^5\ M^{-1}\,s^{-1}$) but is considerably larger than a similar calculated value based upon an experimental rate constant previously determined for the *oxidation* of the corresponding $Cu^I([15]aneS_5)$ complex by an iron(III) complex ($k_{11(Ox)} = 8 \times 10^3\ M^{-1}\,s^{-1}$). These three k_{11} values appear to be consistent with our previous proposal that the Cu(II/I)–polythiaether complexes undergo electron transfer by a dual-pathway "square-scheme" mechanism in which the Cu^IL metastable intermediate species is more stable than the corresponding $Cu^{II}L$ intermediate.

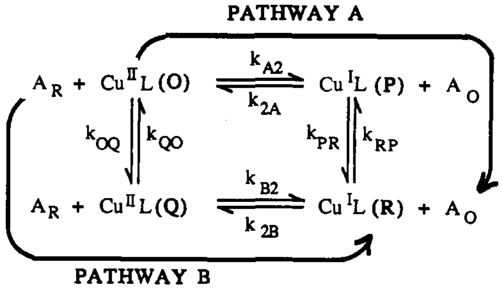
Introduction

In studying the kinetics of electron-transfer reactions involving various Cu(II/I) redox couples with selected counterreagents

$$Cu^{II}L + A_R \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Cu^IL + A_O \tag{1}$$

most investigators have reported only the reduction of $Cu^{II}L$ to Cu^IL (i.e., only k_{12} values have generally been experimentally determined).[2] This reflects the fact that many Cu^IL complexes are of low solubility, are subject to disproportionation, and/or are exceptionally sensitive to air oxidation, and, therefore, are more difficult to control as starting materials. For the few instances in which both the reduction and oxidation of a single redox couple have been reported, however, discrepancies have been noted in the self-exchange rate constant (k_{11}) values which are generated upon applying the Marcus relationship[3] to both the k_{12} and k_{21} values (i.e., $k_{11(Red)} \neq k_{11(Ox)}$).[4,5] This discrepancy is contrary to normal theoretical considerations for outer-sphere electron-transfer processes. Moreover, the direction of the discrepancy appears to depend upon the nature of the complex involved. For

Scheme I



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[1] (a) Wayne State University. (b) University of Wisconsin—Eau Claire.

[2] See, e.g.: Yandell, J. K. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 157-166.

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copper–polypyridyl complexes, for example, $k_{11(\mathrm{Red})} \ll k_{11(\mathrm{Ox})}$[4] whereas the reverse trend has been observed in our laboratory for copper–polythiaether complexes.[5]

In discussing the literature results which had been previously reported for the complexes of copper formed with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy), Lee and Anson[6] suggested that the discrepancies in the calculated k_{11} values obtained from oxidation and reduction studies arise from an unequal contribution of the $\mathrm{Cu^{II}L}$ and $\mathrm{Cu^{I}L}$ species to the overall reorganizational energy. Although they did not expand upon the details of this proposal, they made a subsequent attempt to determine the self-exchange rate constant for the $\mathrm{Cu^{II/I}(phen)_2}$ system using an electrochemical procedure in which the $\mathrm{Cu^{I}L}$ species was adsorbed onto the surface of the electrode.[7] The apparent result indicated that the k_{11} value obtained in this manner was the geometric mean of the corresponding $k_{11(\mathrm{Red})}$ and $k_{11(\mathrm{Ox})}$ values obtained from cross-reactions.

From extensive studies conducted in our laboratory on the copper–polythiaether complexes, we have proposed that the mechanism for electron transfer in these systems can best be described in terms of a dual-pathway mechanism in the form of a "square scheme" (Scheme I) in which the conformational change and the electron-transfer step occur in a sequential, rather than a concerted, manner.[5,8] In this scheme, O and R represent the stable forms of $\mathrm{Cu^{II}L}$ and $\mathrm{Cu^{I}L}$, respectively, Q and P represent metastable intermediates of these same species, and A_R and A_O represent the reduced and oxidized form of any selected counterreagent. The relative stability of the two metastable intermediates determines the preferred reaction pathway: $\mathrm{O} \rightleftharpoons \mathrm{P} \rightleftharpoons \mathrm{R}$ (pathway A) or $\mathrm{O} \rightleftharpoons \mathrm{Q} \rightleftharpoons \mathrm{R}$ (pathway B). Despite the greater complexity of this mechanism, it is still anticipated that $k_{11(\mathrm{Red})} = k_{11(\mathrm{Ox})}$. However, as the reaction potential is increased, the rate of electron transfer may eventually exceed the rate of conformational rearrangement so that the latter step (as represented by the rate constants k_{RP} in the case of pathway A or k_{OQ} for pathway B) can become rate-limiting. Upon a further increase in the reaction potential, the alternate electron-transfer pathway may be made to exceed the rate of the first-order conformational change for $\mathrm{Cu^{I}L}$ *oxidation* (if pathway A is nominally favored) or $\mathrm{Cu^{II}L}$ *reduction* (if pathway B is favored).

For those systems in which the application of the Marcus relationship to oxidation and reduction cross-reaction rate constants yields $k_{11(\mathrm{Red})} \neq k_{11(\mathrm{Ox})}$, analysis of the overall kinetic expressions for Scheme I suggests that the larger of these two values should be equal to the self-exchange rate constant obtained directly from the symmetrical reaction:

$$^{*}\mathrm{Cu^{II}L} + \mathrm{Cu^{I}L} \overset{k_{11(\mathrm{ex})}}{\rightleftharpoons} {}^{*}\mathrm{Cu^{I}L} + \mathrm{Cu^{II}L} \qquad (2)$$

Although values of $k_{11(\mathrm{ex})}$ have been determined directly from NMR line-broadening measurements for a number of low molecular weight copper complexes,[9-14] there appears to be no $\mathrm{Cu^{II/I}L}$ system for which an attempt has been made to correlate the apparent self-exchange rate constant value determined by direct measurements on reaction 2 ($k_{11(\mathrm{ex})}$) to the values obtained by applying the Marcus relationship to cross-reaction rate constants for reaction 1, *as studied in both directions* ($k_{11(\mathrm{Red})}$ and $k_{11(\mathrm{Ox})}$).

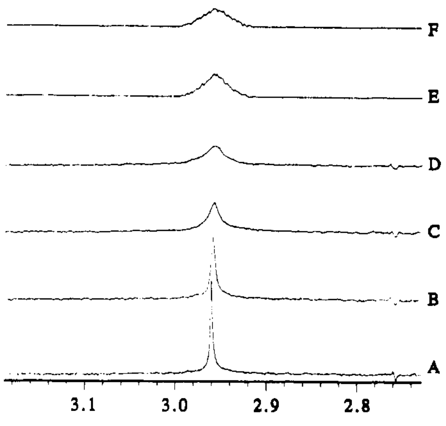
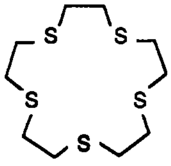


Figure 1. ^{1}H NMR spectrum (uncalibrated) of $\mathrm{Cu^{I}([15]aneS_5)}$ as a function of $\mathrm{Cu^{II}([15]aneS_5)}$ concentration in $\mathrm{D_2O}$ at 25 °C (series VII). For all solutions, $[\mathrm{Cu^{I}L}] = 3.02 \times 10^{-4}$ M and $[\mathrm{Cu^{II}(aq)}] = 0.0010$ M, with $[\mathrm{Cu^{II}L}]$ varied as follows (all values in μM): A, 4.6; B, 28.6; C, 90.9; D, 126; E, 190; F, 236.

To test the validity of the proposed square-scheme mechanism, we have undertaken the direct determination of the self-exchange rate constant value for the Cu(II/I) complex involving the macrocyclic pentathiaether ligand 1,4,7,10,13-pentathiacyclopentadecane, $\mathrm{[15]aneS_5}$, by means of ^{1}H NMR line-broadening measurements. Of the various copper complexes for which values of both $k_{11(\mathrm{Red})}$ and $k_{11(\mathrm{Ox})}$ are available,[4,5] this specific system was chosen for the current study on the basis of its several advantageous properties, including (i) a simple $\mathrm{Cu^{I}L}$ ^{1}H NMR spectrum with a sharp singlet peak (Figure 1), (ii) reasonable stability of the $\mathrm{Cu^{I}L}$ complex with respect to air oxidation, (iii) reasonable thermodynamic stability for the $\mathrm{Cu^{II}L}$ complex,[15] and (iv) simple electrochemical behavior.[16] The NMR studies have been conducted both in $\mathrm{D_2O}$ and in 80% $\mathrm{CD_3OD}$–20% $\mathrm{D_2O}$ (by weight)[17] over a range of temperatures by utilizing variable acidity and reactant concentrations to ensure the veracity of the data. The results are then compared to the self-exchange rate constants previously calculated from cross-reaction kinetic studies in aqueous solution.



$\mathrm{[15]aneS_5}$

Experimental Section

Reagents. Reagent grade copper(II) nitrate was recrystallized twice from water, filtered off, and dried in a vacuum desiccator to yield $\mathrm{Cu(NO_3)_2 \cdot 3H_2O}$. (The waters of crystallization did not significantly affect the NMR spectral data.) Copper metal shot (99.90%, Allied Chemical Corp.), used for the reduction of $\mathrm{Cu^{II}L}$ to the corresponding $\mathrm{Cu^{I}L}$ species, was cleaned with dilute reagent grade nitric acid, rinsed twice with distilled–deionized water, rinsed with methanol, dried in an oven for 2–3 min, and stored in a desiccator for 10 min before use. The synthetic method used to prepare the polythiaether ligand has been previously reported.[18] For the ^{1}H NMR measurements, deuterium oxide (99.8% D) and methanol-d_4 (99.5% D) were obtained from Aldrich Chemical

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(17) It should be noted that both 80% $\mathrm{CD_3OD}$–20% $\mathrm{D_2O}$ and 80% $\mathrm{CH_3OH}$–20% $\mathrm{H_2O}$, as defined on a weight percent basis, are essentially identical in molar composition, both being equivalent to 69% methanol on a mole percent basis.

(18) Ochrymowycz, L. A.; Mak, C.-P.; Michna, J. D. *J. Org. Chem.* **1974**, *39*, 2079–2084.

Co., while chloroform-*d* (99.8% D) was obtained from Stohler Isotope Chemicals.

Preparation of Solutions. Solutions of the $Cu^{II}L$ complexes were prepared by transferring the desired amount of deuterated water (or the appropriate mixture of deuterated water and methanol) to a volumetric flask (sealed with a septum to exclude the condensation of water vapor from the air) which contained a weighed mixture of copper(II) nitrate and the ligand. The resulting solutions were stirred overnight, and their concentrations were checked spectrophotometrically at 25 °C: for $Cu^{II}([15]aneS_5)$, $\epsilon = 6.1 \times 10^3\ M^{-1}\ cm^{-1}$ at 414 nm.

Since the $Cu^{I}L$ complex is stable with respect to disproportionation,[16,19] clean copper shot was used to reduce $Cu^{II}L$ to $Cu^{I}L$ according to the reaction

$$Cu^{II}L + Cu^0 + L \rightarrow 2Cu^{I}L \tag{3}$$

To ensure complete reduction, reaction 3 was carried out overnight under an oxygen-free environment. For solutions containing initially a 1:2 ratio of $[Cu^{II}]:[L]$, the only product obtained was pure $Cu^{I}L$, from which the excess copper shot (and any undissolved solids) could be removed by filtration or decantation. All solutions containing $Cu^{I}L$ and/or $Cu^{II}L$ were stored under oxygen-free argon gas and were transferred from one vessel to another using argon gas pressure or, when necessary, gastight syringes (Hamilton 1000 series). For each series of measurements, five to seven solutions were prepared containing constant amounts of $Cu^{I}L$ but varying concentrations of $Cu^{II}L$. To these solutions was added a measured excess of $Cu(ClO_4)_2$ or $Cu(NO_3)_2$ to diminish the dissociation of the $Cu^{II}L$ species (since this complex is relatively weak).[15] When significant concentrations of $Cu^{II}L$ were added, the amount of Cu(II) salt was decreased accordingly to maintain a constant total amount of Cu(II). The effect of line broadening due to the presence of paramagnetic species was shown to be virtually constant under these conditions. The acidity of all solutions was adjusted to the desired level by the addition of sodium deuterioxide and/or nitric acid-*d* or perchloric acid-*d*, obtained from Sigma Chemical Co. as solutions in D_2O.

Instrumentation. All ^1H NMR spectra for line-broadening experiments and T_1 relaxation measurements were recorded on a Nicolet NT or a GN 300-MHz spectrometer equipped with a variable-temperature unit and an NMC 1280 data system. Other NMR measurements, such as homonuclear decoupling and ^{13}C spectral determinations, were recorded on a Nicolet QE 300-MHz spectrometer. Visible absorption measurements, used to check the concentrations of $Cu^{II}L$ solutions from the NMR tubes, were made using a Cary 17D double-beam recording spectrophotometer with microcuvettes having a 1.00-cm path length. All pH measurements were conducted with an Orion Model 901A digital ionalyzer using a micro Ag/AgCl pH combination electrode. All pD values (i.e., pH in D_2O) were calculated using the standardized scale proposed by Glasoe and Long[20] where the pH meter was standardized using two or three standard aqueous buffers. This scale at 25 °C is expressed as[21]

$$\text{pD} = \text{pH meter reading} + 0.40 \tag{4}$$

Corrections for temperature were not made.

NMR Measurements. A single ^1H peak is observed in D_2O (or, for greater solubility, in $CDCl_3$) for the free ligand at about 2.7 ppm which is shifted further downfield to approximately 2.9 ppm upon complexation to Cu(I) (Figure 1); similar spectra are observed in 80% CD_3OD. For all line-broadening experiments, a one-pulse sequence was used for the acquisition of the free induction decay (FID) signal. The following parameters were employed in this study: 16–100 pulses; 1.5–2.0-s acquisition time; delay time = 1–1.5 s; sweep width (SW) = ±1200 to ±2000 Hz; block size = 8–16K. FID was processed with one zero filling, giving a digital resolution of 0.33–0.44 Hz/point. For two series of solutions in D_2O and for the single series in 80% CD_3OD–20% D_2O, the NMR line-broadening measurements were recorded at four or five temperatures spaced at 10-deg increments.

Shimming on the FID was used in order to ensure a homogeneous field. Field homogeneity was checked using a reference solution containing the sodium salt of (tetramethylsilyl)propionate (TSP) and sodium perchlorate, the latter salt being used to adjust the ionic strength of the reference solution to the same ionic strength as the sample. The line width of the TSP peak was monitored regularly and was constant at 0.75 ± 0.03 Hz throughout the course of the experiment. The peaks were fitted with a Lorentzian function for the determination of the line width. For T_1 relaxation measurements, the inversion recovery (T1IR) method was used[22] yielding a value of T_1 = 0.493 (4) s.[23]

Results

In determining the relaxation times for interconversion between diamagnetic (D) and paramagnetic (P) species

$$D^* + P \rightleftharpoons P^* + D \tag{5}$$

McConnell and Berger[24] derived the following expression from the Bloch equations:

$$k_{11} = \frac{1}{[P]}\left[\left(\frac{1}{T_2}\right)_{DP} - \left(\frac{1}{T_2}\right)_{D}\right] \tag{6}$$

where $(T_2)_D$ is the transverse relaxation time of ^1H for a solution containing only the diamagnetic species and $(T_2)_{DP}$ is the corresponding quantity for a solution containing both the diamagnetic and paramagnetic species, [P] being the concentration of added paramagnetic species. In the derivation of eq 6, the following conditions were assumed: $\tau_D \gg \tau_P$, $((\delta\omega)\tau_P/2)^2 \gg 1$, $\tau_P \gg \tau_p$, and $(T_2)_D \geq \tau_D$, where τ_D and τ_P are the mean lifetimes of the diamagnetic and paramagnetic species, respectively, following electron transfer; τ_p is the paramagnetic spin–lattice relaxation time, $\delta\omega$ is the hyperfine splitting of the electron resonance of the paramagnetic species due to the proton, and $(T_2)_D$ is the spin–spin relaxation time for the diamagnetic species. In treating electron-transfer reactions of the type shown in reaction 2 as a two-site exchange process (i.e., diamagnetic, D, and paramagnetic, P, sites only), McConnell,[25] Swift and Connick,[26] and Dietrich and Wahl[27] (using the equation of Pearson et al.[28]) also derived the same expression under the slow-exchange limit where $\tau_P \gg (T_2)_P$, $(T_1)_P$ and $(T_1)_P$, $(T_2)_P \ll (T_1)_D$, $(T_2)_D$. The terms $(T_1)_P$ and $(T_2)_P$ are the spin–lattice and spin–spin relaxation times, respectively, of the protons in the paramagnetic species, and $(T_1)_D$ is the spin–lattice relaxation time for the diamagnetic species. In the current investigation, it was determined that all of the foregoing conditions were met; thus, it is presumed that eq 6 is valid for the systems reported here.

NMR Spectra. The ^1H NMR spectra for the free ligand and for the corresponding $Cu^{I}L$ complex were recorded using a one-pulse sequence. Due to limited aqueous solubility, the uncomplexed $[15]aneS_5$ was dissolved in $CDCl_3$ and the chemical shift of the singlet ligand peak was located at 2.7 ppm relative to the $CHCl_3$ peak at 7.24 ppm (downfield from external TMS peak). The peak shift for the $Cu^{I}([15]aneS_5)$ complex was recorded at 2.9 ppm using both D_2O and 80% CD_3OD–20% D_2O (w/w) as solvent with the chemical shift reported relative to the HOD peak at 4.8 ppm (downfield from external TSP peak). The appearance of only a single ^1H resonance line (Figure 1) indicates that all of the protons are chemically and magnetically equivalent, which might appear to suggest that all five sulfur donor atoms are coordinated to Cu^{I} in a symmetrical array. However, five-coordinate $Cu^{I}L$ is relatively rare[11,29,30] and the only symmetrical five-coordinate geometry would be that of a pentagonal plane, which is extremely unlikely. Moreover, the crystal structure for the $Cu^{I}L$ complex indicates that only four sulfur donor atoms are coordinated to yield a tetrahedral geometry.[31] Therefore, the

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observed single peak in the ^1H spectrum for Cu^IL is interpreted to result from a rapid Cu–S bond breaking and bond forming involving all five sulfur atoms, giving an average resonance line. In support of this interpretation, it has been observed that the line width at half-height of this peak decreases with increasing temperature. This narrowing of the line is expected as the rate of bond breakage and bond formation increases with increasing temperature.

Determination of Self-Exchange Rate Constants. As noted above, the self-exchange rate constant for each series of solutions was determined using the line-broadening technique in which the value of the Cu^IL resonance line width was measured as a function of the concentration of added $Cu^{II}L$. In all cases, the value of $[Cu^{II}L]$ was experimentally determined from spectrophotometric absorbance measurements. In the calculation of the $k_{11(ex)}$ values, eq 6 was used in the following modified form:

$$W_{DP}Q\pi = W_DQ_\pi + k_{11(ex)}[Cu^{II}L] \quad (7)$$

In this expression, W_{DP} is the peak width at half-height ($T_2^{-1} = \pi W_{1/2}$) of the single proton resonance peak from a solution containing both the diamagnetic (Cu^IL) and paramagnetic ($Cu^{II}L$) species, W_D is the corresponding value for a solution containing only the diamagnetic species, and Q is a factor used to correct the extent of outer-sphere complex formation at the specific ionic strength used (represented by the outer-sphere equilibrium constant $K_{OS(s)}$) to a common ionic strength value of 0.10 M (represented by the constant $K_{OS(0.1)}$):[32]

$$Q = K_{OS(0.1)}/K_{OS(s)} \quad (8)$$

where

$$K_{OS} = \frac{4\pi N_A a^3}{3000} \exp\left[\frac{Z_A Z_B e_0^2}{Dk_BT}\left(\frac{1}{a'} - \frac{\kappa}{1 + \kappa a'}\right)\right] \quad (9)$$

$$\kappa = \left(\frac{8\pi N_A e_0^2 \mu}{1000Dk_BT}\right)^{1/2} \quad (10)$$

In these expressions, N_A represents Avogadro's number, a is the center-to-center distance of closest approach (in cm) in the formation of the outer-sphere complex between Cu^IL and $Cu^{II}L$ preceding electron transfer, Z_A and Z_B are the formal charges on the two complex species (+2 and +1 in the current system), e_0 is the electronic charge (in esu), D is the dielectric constant of the solvent medium, k_B is the Boltzmann constant (in erg K^{-1} mol^{-1}), T is the absolute temperature (in K), a' is the distance (in cm) between the charge centers in the outer-sphere complex, and μ is the ionic strength. The radii of Cu^IL and $Cu^{II}L$ were previously determined to be approximately 4.4×10^{-8} cm,[5] their sum (i.e., 8.8×10^{-8} cm) being used for both a and a' in the current work.

As a result of the relatively low thermodynamic stability of the $Cu^{II}([15]aneS_5)$ complex,[15,33] an excess of the aquocopper(II) ion was added to all solutions in order to shift the complex formation equilibrium to the right:

$$Cu^{II}(aq) + L \rightleftharpoons Cu^{II}L \quad (11)$$

In this regard, three general sets of conditions were utilized: (i) $[Cu^{II}(aq)] = 0.10$ M, which ensured complete formation of $Cu^{II}L$ but resulted in relatively broad peaks due to the paramagnetic effect (reducing the relative percentage of line broadening); (ii) $[Cu^{II}(aq)] \approx 1.0 \times 10^{-3}$ M, which reduced the total line width but resulted in only about 93–94% formation of $Cu^{II}L$; and (iii) $[Cu^{II}(aq)] \approx 1 \times 10^{-4}$ M, which resulted in only about 10% formation of $Cu^{II}L$.[15] The addition of $Cu^{II}(aq)$ up to 0.10 M to a solution containing only Cu^IL resulted in uniform broadening of the Cu^IL spectrum in all solutions (see supplementary material).[34] The similarities in the $k_{11(ex)}$ values obtained for different series of measurements with varying amounts of added $Cu^{II}(aq)$ indicates that no electron transfer occurred between $Cu^{II}(aq)$ and Cu^IL on the NMR time scale.

Seven series of measurements were made, one in which 80% CD_3OD–20% D_2O (by weight) was used as the solvent and six in which the solvent was pure D_2O. The specific experimental line width data are given in the supplementary material. A typical plot of the data for one series of measurements conducted in D_2O is shown in Figure 2. The results of the variable-temperature

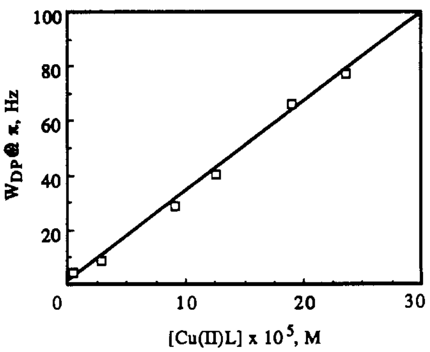

Figure 2. Plot of eq 13 for the peak width data obtained from the series of solutions (series VII) shown in Figure 1. The slope of the regression line is 3.29×10^5 M^{-1} s^{-1}.

Table I. Self-Exchange Rate Constant Values Determined for the $Cu^{II/I}([15]aneS_5)$ System at Variable Temperature, Corrected to 0.10 M Ionic Strength[a]

	$10^{-4}k_{11}$, M^{-1} s^{-1}		
T, °C	series I[b] 80% CD_3OD, pD = 2.66	series II[c] D_2O, pD = 3.32	series III[d] D_2O, pD = 4.3
−5	3.01 (12)		
5	4.51 (10)	3.95 (11)	7.8 (5)
15	5.87 (14)	5.6 (2)	9.9 (5)
25	8.3 (3)	7.4 (2)	11.6 (6)
35		9.1 (2)	13.7 (6)
45		11.5 (3)	16.8 (12)

[a] For this and subsequent tables, values in parentheses represent the standard deviation for the last digit(s) listed; thus, 3.01 (12) and 16.8 (12) represent 3.01 ± 0.12 and 16.8 ± 1.2, respectively. [b] Series I: $[Cu^IL] = 1.02$ mM; $[Cu^{II}L]_{max} = 0.048$ mM; $[Cu^{II}(aq)] = 0.10$ mM. [c] Series II: $[Cu^IL] = 0.78$ mM; $[Cu^{II}L]_{max} = 0.036$ mM; $[Cu^{II}(aq)] = 0.11$ mM. [d] Series III: $[Cu^IL] = 7.6$ mM; $[Cu^{II}L]_{max} = 0.12$ mM; $[Cu^{II}(aq)] = 0.10$ mM.

Table II. Summary of NMR Line-Broadening Determinations of the $Cu^{II/I}([15]aneS_5)$ Self-Exchange Rate Constant at 25 °C, Corrected to 0.10 M Ionic Strength

series	$[Cu^IL]$, mM	$[Cu^{II}L]_{max}$, mM	$[Cu^{II}(aq)]$, M	solvent	pD	$10^{-5}k_{11}$, M^{-1} s^{-1}
I	1.02	0.048	0.00010	80% CD_3OD	2.66	0.83 (3)
II	0.78	0.036	0.00011	D_2O	3.32	0.74 (2)
III	7.6	0.12	0.10	D_2O	4.3	1.16 (6)
IV	0.198	0.16	0.10	D_2O	2.8	2.16 (8)[a]
V	0.322	0.24	0.10	D_2O	2.8	2.24 (6)
VI	0.395	0.25	0.0010	D_2O	5.4	3.32 (6)
VII	0.302	0.24	0.0010	D_2O	2.2	3.29 (12)

[a] For series IV, line width measurements were actually made at 20 °C to give $k_{11} = 1.93\ (\pm 0.06) \times 10^5$ M^{-1} s^{-1}; this value was corrected to the 25 °C value listed in the table using the mean activation parameters determined from series II and III.

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(31) 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.

(32) Lin, C.-T.; Rorabacher, D. B. *Inorg. Chem.* **1973**, *12*, 2402–2410.

(33) Young, I. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1986**, *25*, 2576–2582.

(34) From blank measurements, it was apparent that, under the experimental conditions used, the maximum amount of $Cu^{II}L$ added in obtaining our measurements did not significantly affect the paramagnetic line broadening. In many cases, however, the total value of $[Cu^{II}(aq)]$ + $[Cu^{II}L]$ was maintained at a constant value to ensure constant line broadening due to the paramagnetic ion effect.

Table III. Activation Parameters for the $Cu^{II/I}([15]aneS_5)$ Self-Exchange Rate Constant, Corrected to 0.10 M Ionic Strength

series	solvent	ΔH^*, kJ mol^{-1}	ΔS^*, J K^{-1} mol^{-1}
I	80% CD_3OD	19.6 (11)	−77 (4)
II	D_2O	16.9 (8)	−95 (4)
III	D_2O	11.2 (5)	−110 (3)

studies are given in Table I, with a summary of the 25 °C results for all seven studies presented in Table II. All values listed are corrected to 0.10 M ionic strength.

Discussion

Self-Exchange Rate Constant Value and Activation Parameters. The experimental data for this investigation were acquired with two different NMR spectrometers, different experimentalists, different solvent matrices, a 10-fold range in the concentration of Cu^IL, a 1000-fold range in the amount of excess $Cu^{II}(aq)$, and a 1000-fold range in acidity. Thus, it is not surprising that there is some variation in the data. Nevertheless, the 25 °C $k_{11(ex)}$ values obtained for the $Cu^{II/I}([15]aneS_5)$ system are reasonably consistent for all seven series (Table II). In particular, the fact that the resolved $k_{11(ex)}$ value appears to be independent of the acidity level provides a strong indication that electron transfer is occurring by an outer-sphere mechanism, since the hydroxide (i.e., deuterioxide) ion is the only bridging ligand present in these solutions.

In view of the relatively small complex formation constant for $Cu^{II}([15]aneS_5)$, series III–V (Table II), involving a large excess of $Cu^{II}(aq)$ (0.1 M), are considered to represent more ideal conditions, since the $Cu^{II}L$ complex is essentially fully formed under these conditions—although the broader peaks caused by the very high concentration of paramagnetic ion result in a slight decrease in precision. Correction of the series IV data (obtained at 20 °C) to 25 °C results in a $k_{11(ex)}$ value nearly identical to that obtained from series V (Table II). The mean value calculated from series III–V is $k_{11(ex)} = 1.9\ (\pm 0.6) \times 10^5\ M^{-1}\ s^{-1}$ at 25 °C whereas the mean of all six aqueous series (series II–VII) is $k_{11(ex)} = 2.2\ (\pm 1.1) \times 10^5\ M^{-1}\ s^{-1}$. Thus, we conclude that $k_{11(ex)} \approx 2 \times 10^5\ M^{-1}\ s^{-1}$ at 25 °C.

For series I–III, the variable-temperature data were plotted according to the Arrhenius equation in the form

$$\ln k_{11(ex)} = \ln A - E_a/RT \qquad (12)$$

where A is the Arrhenius frequency factor, E_a is the activation energy, and R is the universal gas constant. The values of ΔH^* and ΔS^* were then calculated according to the relationships (for reactions in solution)[35]

$$\Delta H^* = E_a - RT + P\Delta V^* \approx E_a - 2.5\ \text{kJ mol}^{-1} \qquad (13)$$

$$\Delta S^* = R[\ln k_{11(ex)} - \ln (k_BT/h)] + \Delta H^*/T \qquad (14)$$

where h represents Planck's constant. The resulting activation parameters calculated for these three series are listed in Table III. Combining the results obtained from series II and III yields $\Delta H^* = 14.0 \pm 4.0$ kJ mol^{-1} and $\Delta S^* = 103 \pm 11$ J K^{-1} mol^{-1} for an aqueous solution.

Mechanistic Significance. The crystallographic structures which have been determined for $Cu^{II}([15]aneS_5)$ and $Cu^I([15]aneS_5)$[31] indicate that the Cu(II) ion in the former complex is coordinated only to the five sulfur donor atoms, one of these Cu–S bonds being ruptured upon reduction to Cu(I); changes in the remaining bond distances and angles are relatively small. We suggest that little energy is required to break one Cu–S bond during the reduction process. The small difference in the stability of the $Cu^{II}([15]aneS_5)$ complex relative to the corresponding macrocyclic tetrathiaether complexes[15,33] indicates that the fifth Cu–S bond is weak. Moreover, Stanbury and Scheidt and co-workers[11b] recently determined the self-exchange electron-transfer rate constant (in CD_3CN) for a copper complex in which the copper ion remains five-coordinate in both oxidation states and obtained values of $\Delta H^* = 16.2 \pm 3.3$ kJ mol^{-1} and $\Delta S^* = -103 \pm 12$ J K^{-1} mol^{-1} (in CD_3CN); these results are virtually identical to the values obtained in this work. Thus, it is apparent that the Cu–S bond rupture does not contribute significantly to the energetics of the electron-transfer process for the current system.[36]

In our earlier studies involving cross-reactions of copper–polythiaether complexes with selected counterreagents (reaction 1), we applied the Marcus relationship to both the reduction and oxidation reactions (i.e., to both k_{12} and k_{21}) in order to obtain estimates of the self-exchange rate constant, k_{11}.[5] The resulting values for $Cu^{II/I}([15]aneS_5)$ at 25 °C, $\mu = 0.10$, differed by about 40-fold: $k_{11(Red)} = 3 \times 10^5\ M^{-1}\ s^{-1}$ and $k_{11(Ox)} = 8 \times 10^3\ M^{-1}\ s^{-1}$. The mean value of $k_{11(ex)} \approx 2 \times 10^5\ M^{-1}\ s^{-1}$ obtained in the current study is clearly within experimental error of the higher value, $k_{11(Red)}$.

As noted earlier, we have previously proposed that the mechanism for electron transfer involving the Cu(II/I)–polythiaether complexes can be described in terms of a square scheme (Scheme I) in which the preferred pathway, under conditions of low driving force, is that designated as pathway A. Under these conditions, the "pure" self-exchange reaction can be described as

$$^*O + P \rightleftharpoons {}^*P + O \qquad (15)$$

where, as defined previously, O represents the stable form of $Cu^{II}L$ and P represents the metastable form of Cu^IL. In the current work, we have treated the self-exchange reaction in terms of the concentrations of the two stable forms:

$$r_{ex} = k_{11(ex)}[O][R] \qquad (r = \text{rate}) \qquad (16)$$

To express this exchange in terms of the metastable form of Cu^IL, we must invoke the equilibrium constant $K_{PR} = [R]/[P]$, i.e.

$$r_{ex} = k_{11(ex)}K_{PR}[O][P] = k_{11(ex)}'[O][P] \qquad (17)$$

Thus, the specific self-exchange rate constant for reaction 15, $k_{11(ex)}'$, should differ from the value obtained in the current work by the magnitude of the conformational equilibrium constant, K_{PR} (Scheme I). This latter equilibrium constant has been estimated[37] to have a value of approximately 30 for $Cu^I([14]aneS_4)$ in 80% CH_3OH at 25 °C but has not yet been determined for $Cu^{II/I}([15]aneS_5)$. However, as noted below, the availability of this equilibrium constant is not essential for analyzing the mechanistic behavior under conditions where species P and R are equilibrated.

Implications of the Marcus Cross Relation Calculations. For cross-reactions involving the *reduction* of $Cu^{II}L$ with a selected counterreagent, A_R, the Marcus equation can be written in the form[3]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (18)$$

where k_{22} represents the self-exchange rate constant for the counterreagent, K_{12} (eq 19) represents the equilibrium constant

$$K_{12} = \exp[(E_1{}^f - E_2{}^f)n\mathcal{F}/RT] \qquad (19)$$

for reaction 1, $E_1{}^f$ and $E_2{}^f$ are the formal potential values for the $Cu^{II}L/Cu^IL$ and A_O/A_R redox couples, respectively, n is the number of electrons transferred, $\mathcal{F}$ is the Faraday constant; and the terms f_{12} and W_{12} represent the nonlinear and work term

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(35) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice-Hall: Englewood Cliffs, NJ, 1989; pp 322–323.

(36) Although a direct measurement of the kinetics of Cu–S bond rupture and formation has not been made for the $Cu^{II/I}([15]aneS_5)$ system, these processes are presumed to be extremely rapid. In the case of $Cu^{2+}(aq)$, Cu–S bond formation (in the outer-sphere complex) should be about $2 \times 10^9\ s^{-1}$ at 25 °C (Sokol, L. S. W. L.; Fink, T. D.; Rorabacher, D. B. *Inorg. Chem.* **1980**, *19*, 1263–1266). This large value is partly the result of the weak axial bonding due to Jahn–Teller distortion, and the removal of orbital degeneracy in the current system may be presumed to decrease this value by about 2–3 orders of magnitude (Moss, D. B.; Lin, C.-T.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1973**, *95*, 5179–5185). All evidence suggests that the internal bond rotations associated with the Cu–S bond rupture–formation process in $Cu^{II/I}([15]aneS_5)$ should also be relatively rapid (Diaddario, L. L.; Zimmer, L. L.; Jones, T. J.; Sokol, L. S. W. L.; Cruz, R. B.; Yee, E. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3511–3520).

(37) Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. To be submitted for publication.

corrections, respectively, as defined elsewhere.[5] In applying eq 18 to our earlier cross-reaction studies, we utilized the thermodynamic value of E_1^f corresponding to the $Cu^{II}L(O)/Cu^{I}L(R)$ redox couple, and therefore, the self-exchange rate constant $k_{11(Red)}$ should correlate to the value of $k_{11(ex)}$ determined in this work as defined by eq 16. By contrast, if the initial reduction product of the cross-reaction is taken to be $Cu^{I}L(P)$, then the value of $k_{11(ex)}'$, as defined in eq 17, can be utilized in eq 18 along with the corresponding value of K_{12}' based on the $Cu^{II}L(O)/Cu^{I}L(P)$ redox couple, using the O/P potential value, designated as E_{OP}^f:

$$K_{12}' = \exp[(E_{OP}^f - E_1^f)n\mathcal{F}/RT] \tag{20}$$

For the condition where $K_{PR} \gg 1$ (and $K_{OQ} \ll 1$), which appears to apply to related copper–polythiaether systems,[8] it can readily be shown that[16]

$$E_{OP}^f = E_1^f - (RT/n\mathcal{F}) \ln K_{PR} \tag{21}$$

Combining eqs 20 and 21 or using simple thermodynamic arguments, one sees that

$$K_{12}' = K_{12}/K_{PR} \tag{22}$$

Thus, the use of K_{12}' and $k_{11(ex)}'$ in place of K_{12} and $k_{11(ex)}$ in eq 18 yields the same result, since the K_{PR} term cancels out.

For oxidations occurring by pathway A, where the equilibrium step $R \rightleftharpoons P$ precedes the rate-determining electron-transfer process, the general kinetic expression can be written as (for conditions where $K_{PR} \gg 1 \gg K_{OQ}$)[5,8]

$$\frac{d[Cu^{II}L]}{dt} = \left(\frac{k_{2A}k_{RP}}{k_{2A}[A_O] + k_{PR}} + k_{2B}\right)[R][A_O] \tag{23}$$

Three limiting rate expressions may be generated from eq 27:

$$d[Cu^{II}L]/dt = K_{PR}^{-1}k_{2A}[R][A_O] \tag{24}$$

$$d[Cu^{II}L]/dt = k_{PR}[R] \tag{25}$$

$$d[Cu^{II}L]/dt = k_{2B}[R][A_O] \tag{26}$$

Equation 24 represents the fully equilibrated condition for which the calculated value of $k_{11(Ox)}$ should be identical to $k_{11(ex)}$. The limiting condition leading to eq 25 involves the first-order conformational change $R \rightarrow P$ as the rate-determining step, resulting in a first-order process. The third expression, eq 26, represents the limiting condition in which pathway B has now become dominant for the oxidation process. Since the oxidation cross-reaction previously reported for this system[5] exhibited second-order kinetic behavior, either eq 24 or eq 26 must apply. It should be noted that eq 24 is equivalent to

$$d[Cu^{II}L]/dt = k_{2A}[P][A_O] \tag{24'}$$

Recognizing the equivalency of two forms of the Marcus expression

$$k_{2A} = (k_{11}'k_{22}K_{21}'f_{21}')^{1/2}W_{21} \tag{27a}$$

$$k_{21} = (k_{11}k_{22}K_{21}f_{21})^{1/2}W_{21} \tag{27b}$$

where K_{21} and K_{21}' are the reciprocals of K_{12} and K_{12}', respectively, we conclude that the calculated values of $k_{11(Ox)}$ and $k_{11(Ox)}'$ should be identical to the values calculated for $k_{11(Red)}$ and $k_{11(Red)}'$, respectively, if eq 24 applies. Since $k_{11(Ox)} \ll k_{11(Red)}$, it is presumed that eq 26 applies to the observed oxidation; that is, the oxidation reaction observed in the previous study[5] apparently occurred via pathway B.

Conclusions. The results of the current study reveal that, for the $Cu^{II/I}([15]aneS_5)$ system, $k_{11(ex)} \approx k_{11(Red)} \gg k_{11(Ox)}$, the last two values being calculated from the application of the Marcus relationship to the rate constants previously obtained for selected cross-reactions. These results contradict the prediction of Lee and Anson[6] that, for $Cu^{II/I}L$ systems, the value of $k_{11(ex)}$ should be intermediate between the values of $k_{11(Red)}$ and $k_{11(Ox)}$.

The behavior observed in the current work is consistent with the predictions of the square-scheme mechanism (Scheme I) under conditions where pathway A is nominally preferred, provided that the cross-reaction involving the oxidation of the $Cu^{I}L$ complex was conducted under the limiting condition in which the rate of exchange via pathway B exceeds the rate of conformational change of the $Cu^{I}L$ species. This demonstrated change in kinetic behavior appears to confirm the hypothesis that this $Cu^{II/I}L$ system is capable of exhibiting "gated" electron transfer as defined by Hoffman and Ratner[38] and by Brunschwig and Sutin[39] for reactions involving metastable intermediate species. We propose that this may, in fact, be a common phenomenon for many (if not most) $Cu^{II/I}L$ systems with the direction of the "gating" being dependent upon the structural constraints of the individual system. It should be noted, however, that the theoretical analyses presented by Brunschwig and Sutin regarding the complexities involved in such electron-transfer mechanisms suggest that several unusual phenomena may result, depending upon the relative stabilities of the metastable intermediates. Thus, it would appear that further experimental investigations of the electron-transfer behavior of a variety of Cu(II/I) systems are warranted before a more definitive conclusion can be reached regarding this phenomenon.

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Supplementary Material Available: Tables containing original experimental line width data for line-broadening measurements (5 pages). Ordering information is given on any current masthead page.

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(38) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237–6243.

(39) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454–7465.