# Electron-Transfer Kinetics and Thermodynamic Characterization of Copper(II/I) Complexes with Acyclic Tetrathiaethers in Aqueous Solution

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The kinetics of a series of Cu(II/I)−acyclic tetrathiaether complexes reacting with several oxidizing and reducing reagents have been examined in aqueous solution at 25 °C. This investigation has included a re-examination of $\mathrm{Cu^{II/I}(Me_2\text{-}2,3,2\text{-}S_4)}$ ($\mathrm{Me_2\text{-}2,3,2\text{-}S_4}$ = 2,5,9,12-tetrathiatridecane = L12a), containing the ethylene−trimethylene−ethylene bridging sequence, plus three newly synthesized ligands containing an alternate bridging sequence of trimethylene−ethylene−trimethylene: 2,6,9,13-tetrathiatetradecane ($\mathrm{Me_2\text{-}3,2,3\text{-}S_4}$ = L12b) and two cyclohexanediyl-substituted derivatives, *viz.*, *cis*-1,2-bis[(3-methylthiopropyl)thio]cyclohexane (*cis*-cyhx-$\mathrm{Me_2\text{-}3,2,3\text{-}S_4}$ = L14) and *trans*-1,2-bis[(3-methylthiopropyl)thio]cyclohexane (*trans*-cyhx-$\mathrm{Me_2\text{-}3,2,3\text{-}S_4}$ = L15). The corresponding phenylene derivative, 1,2-bis[(3-(methylthio)propyl)thio]benzene (bz-$\mathrm{Me_2\text{-}3,2,3\text{-}S_4}$ = L13), was also synthesized but did not form a measurable copper complex. The conditional stability constants for $\mathrm{Cu^{II}L}$ ($K_{\mathrm{Cu^{II}L'}}$) and $\mathrm{Cu^{I}L}$ ($K_{\mathrm{Cu^{I}L'}}$) and the $\mathrm{Cu^{II/I}L}$ formal redox potentials ($E^{\mathrm{f}}$) vs NHE at 25 °C (generally at $\mu = 0.10$ ($\mathrm{NaClO_4}$)) are as follows: for L12b, 15 $\mathrm{M^{-1}}$, $1.0 \times 10^{13}$ $\mathrm{M^{-1}}$, 0.83 V; for L14, $2.8 \times 10^{2}$ $\mathrm{M^{-1}}$, $0.9_5 \times 10^{13}$ $\mathrm{M^{-1}}$, 0.75 V; for L15, $8.8 \times 10^{2}$ $\mathrm{M^{-1}}$, $6._3 \times 10^{13}$ $\mathrm{M^{-1}}$, 0.77 V. Application of the Marcus relationship to the experimentally determined cross-reaction rate constants yielded self-exchange rate constants for all four $\mathrm{Cu^{II/I}L}$ acyclic systems which were relatively constant for both oxidation and reduction under a wide range of conditions. This contrasts sharply with previous results obtained for corresponding macrocyclic ligand systems.

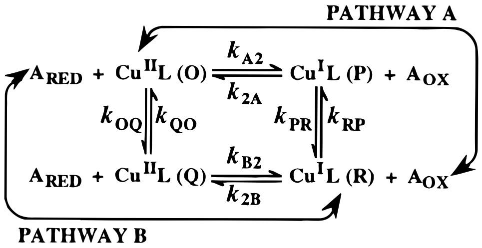
## Introduction

In several previous studies involving both the oxidation and reduction kinetics of a series of copper(II/I)−macrocyclic polythiaether complexes[2−9]

$$\mathrm{Cu^{II}L + A_{Red}} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \mathrm{Cu^{I}L + A_{Ox}} \qquad (1)$$

we have noted that the application of the Marcus relationship[10] to the rate constants obtained for $\mathrm{Cu^{II}L}$ reduction ($k_{12}$) tend to yield apparent $\mathrm{Cu^{II}L/Cu^{I}L}$ self-exchange rate constants which are several orders of magnitude larger than the corresponding values calculated from $\mathrm{Cu^{I}L}$ oxidation rate constants ($k_{21}$). This seemingly anomalous behavior has been attributed to the fact that part of the conformational change is occurring sequentially, rather than concertedly, with the electron-transfer step. Since conformational change and electron-transfer may occur in either order, the proposed mechanism has been formulated as a dual-pathway square scheme involving metastable intermediates for both the $\mathrm{Cu^{I}L}$ and $\mathrm{Cu^{II}L}$ species, designated as P and Q, respectively, in Scheme 1. Cyclic voltammetric studies on $\mathrm{Cu^{II/I}([14]aneS_4)}$ (the macrocyclic tetrathiaether with optimal cavity size; see Figure 1)[11,12] and several cyclohexanediyl derivatives[13] have provided direct evidence for such intermediates and permitted evaluation of all stepwise rate constants in Scheme 1.

**Scheme 1**



The behavior observed in the foregoing studies is consistent with the theoretical model for dual-pathway mechanisms as described by both Hoffman and Ratner[14,15] and by Brunschwig and Sutin.[16,17] This includes the onset of first-order behavior for some oxidations, independent of the counter reagent concentration, attributable to "conformational gating".[14] With

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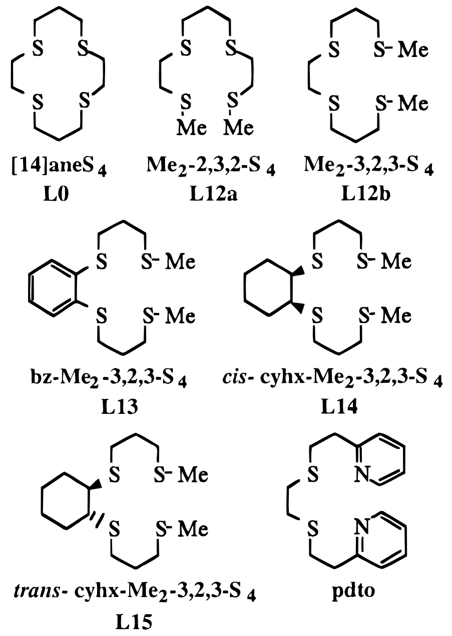


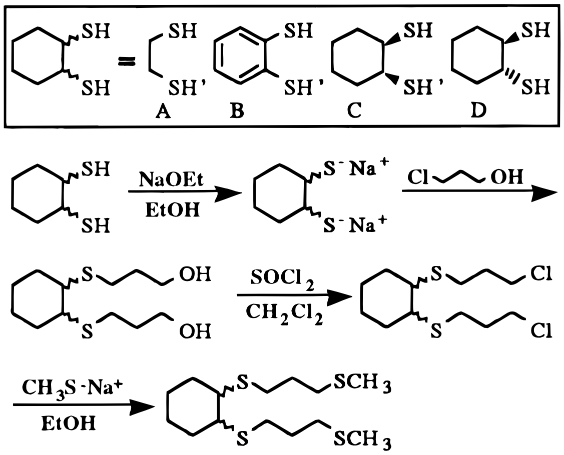
**Figure 1.** Ligands discussed in this work.

further increases in driving force, the alternate pathway can become dominant, yielding a smaller self-exchange rate constant value. Thus, the observed generation of distinctly different self-exchange rate constants for oxidation ($k_{11(\mathrm{Ox})}$) and reduction ($k_{11(\mathrm{Red})}$) reactions, under appropriate reaction conditions, is also characteristic of a dual-pathway mechanism.

The two acyclic ligand systems included in our original study appeared to exhibit larger $k_{11(\mathrm{Red})}/k_{11(\mathrm{Ox})}$ ratios than did any of the macrocyclic ligand systems.[2] From molecular models it is obvious that acyclic ligands are more flexible than similar macrocyclic species and can readily adapt to either the planar coordination preferred by Cu(II) or the tetrahedral coordination normally exhibited by Cu(I).[18] Although this should result in larger conformational changes, the energy barriers should be smaller—since intraligand rotations are less restricted—implying that the onset of conformationally-gated behavior would be less likely to be observed. These considerations suggested that a more thorough investigation of Cu(II/I)—acyclic ligand complexes was warranted.

In the current study, we have re-examined both the oxidation and reduction kinetics of one of the two acyclic ligand systems included in the original survey, $\mathrm{Cu^{II/I}(Me_2\text{-}2,3,2\text{-}S_4)}$—possessing an ethylene—trimethylene—ethylene (i.e., 2,3,2) bridging sequence—as well as the corresponding ligand with a trimethylene—ethylene—trimethylene (i.e., 3,2,3) bridging sequence. These two ligands are of particular interest as they represent the two acyclic analogues of $[14]\mathrm{aneS_4}$, in which the macrocycle has been opened at either a trimethylene bridge or an ethylene bridge. Unfortunately, kinetic studies on both of these systems are hampered by very small $\mathrm{Cu^{II}L}$ stability constants. In an attempt to overcome this difficulty, three derivatives of $\mathrm{Me_2\text{-}3,2,3\text{-}S_4}$ have also been synthesized in which the central ethylene bridge has been replaced by 1,2-phenylene or by *cis*- or *trans*-1,2-cyclohexane. For all five acyclic ligands, terminal methyl groups were utilized to minimize steric hindrance effects. For ease of reference, all five ligands have been assigned number designations (L12a, L12b, L13, L14 and L15, respectively—see Figure 1) consecutive with numbers assigned to a series of related macrocyclic ligands recently reported.[19]

**Scheme 2**



## Experimental Section

**General Approach to Synthone Intermediates and Ligands.** The approach utilized for synthesizing $\mathrm{Me_2\text{-}2,3,2\text{-}S_4}$ (L12a) has been previously described.[20] Scheme 2 illustrates the generalized synthetic strategy exploited for the 3,2,3-bridged ligands investigated in this study. We have previously documented the preparation of the essential 1,2-dithiol synthones (B—D) and both the bis(3-hydroxypropyl) sulfides and bis(3-chloropropyl) sulfide intermediates.[19] This scheme offers the advantage that the bis(3-chloropropyl) sulfide intermediates are stable $\gamma$-chloro sulfides which pose minimal vesicant hazard. The sodium methanethiolate reagent, utilized in the last step, was prepared fresh for each application of Scheme 2 and requires the precaution of a highly efficient fume hood throughout for handling the high toxicity and stench of methanethiol (170 g reagent lecture cylinder, Aldrich Chemical Co.). Approximately 0.5 molar sodium methanethiolate solutions were prepared to reaction scale in absolute ethanol as described below for L12b. Commercially available starting compounds were used as obtained from Aldrich. Reagent solvents for synthesis were obtained from Fisher Scientific or EM Science and were used without further purification.

**General Separation and Characterization Techniques.** The crude ligand products were purified by several vacuum distillations with a standard Kugelrohr apparatus. TLC assays were performed on 1 × 3 in., 250 $\mu$m, MK6F Whatman glass plates and observed by UV contrast at 254 nm or iodine vapor staining. Solvent mixtures are reported as volume per cent. Further product purity assays and characterizations were achieved by the following spectral data: FT-IR (Nicolet 5 DXC), all as neat liquids; $^1$H- and $^{13}$C-NMR spectra, only $^{13}$C data reported, since the overlapping $^1$H-NMR patterns of the ligand series offer little *a priori* basis for distinction. Carbon environments were assigned by 1D-DEPT analysis. GC-mass spectrometry (Hewlett-Packard 5971A, EI/CI mass selection detector, HP-5890 Series II GC system, with HP-5 capillary column) determinations were carried out on dilute ether solutions at 200 °C injector temperatures and rapid temperature ramps

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**Table 1.** Experimentally Determined Redox Potentials, Conditional Stability Constants, and Spectral Parameters for the Copper(II/I)−Acyclic Tetrathiaether Complexes in Aqueous Solution at 25 °C, $\mu = 0.10$ M ($ClO_4^-$) (Except As Noted)

| complexed ligand | $E^f$, V vs NHE | $K_{Cu^{II}L'}$, $M^{-1}$ | $K_{Cu^{I}L'}$,[a] $M^{-1}$ | $\lambda_{max}$, $M^{-1}$ | $10^{-3}\epsilon_{Cu^{II}L}$, $M^{-1}$ $cm^{-1}$ |
|---|---|---|---|---|---|
| [14]ane$S_4$ (L0) | 0.58[b] | $2.1_8 \times 10^4$ [c] | $1.3 \times 10^{12}$ | 390[c] | 8.04[c] |
| $Me_2$-2,3,2-$S_4$ (L12a) | 0.79[b,d] | $0.94 \times 10^2$ [c] | $1._3 \times 10^{13}$ | 407[c] | 7.87[c] |
| $Me_2$-3,2,3-$S_4$ (L12b) | 0.83 [d] | $0.15(1) \times 10^2$ | $1._0 \times 10^{13}$ | 412 | 7.98 |
| *cis*-cyhx-$Me_2$-3,2,3-$S_4$ (L14) | 0.75 | $2.8(1) \times 10^2$ | $0.9_5 \times 10^{13}$ | 418 | 6.72 |
| *trans*-cyhx-$Me_2$-3,2,3-$S_4$ (L15) | 0.77 | $8.8(5) \times 10^2$ | $6._3 \times 10^{13}$ | 407 | 7.90 |

[a] Calculated using eq 5. [b] Bernardo, M. M.; Heeg, M. J.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1992**, *31*, 191−198 (see Table III, footnote c). [c] Reference 22. [d] Determined in this work using solutions containing 0.10 M $Cu(ClO_4)_2$ ($\mu = 0.30$, $[ClO_4^-] = 0.20$ M).

up to 280 °C without decomposition of samples. The reported parent ($M^+$) and base peak values correspond to the lowest mass sulfur isotope values. Elemental analyses were in agreement with the theoretical compositions for all four ligands.

**Generalized Condensation Procedure Documented for 2,6,9,13-Tetrathia-tetradecane ($Me_2$-3,2,3-$S_4$ = L12b).** A mantle-heated, three-necked, 1-L flask was fitted with a 1-in. magnetic stirrer, argon gas inlet adapter, and Friedrich condenser, through which was vented the argon gas sweep to an oil bubbler at about 2 mL min$^{-1}$. The center port of the flask was used for addition of reactants when not sealed with a glass stopper. The flask was charged with 250 mL of absolute ethanol and 3 g (0.13 mol) of freshly cut sodium was added in small pieces over 1 h to generate a sodium ethoxide solution. Methanethiol was then injected into the solution at a minimum positive pressure gas flow rate through a fritted glass gas-dispersion tube (Aldrich), while the 7.2 g (0.15 mol) delivered was monitored by weight change of the gas lecture cylinder. To this solution was added in rapid dropwise fashion 14.75 g (0.06 mol) of 1,10-dichloro-4,7-dithiadecane in 50 mL of ethanol. The reaction was allowed to reflux for 2 h, cooled to 5 °C and vacuum filtered to remove precipitated salt. The filtrate was rotary vacuum evaporated and the residue taken up in 200 mL of ether. The ether solution was washed twice with 100 mL of 5% sodium hydroxide, dried with $MgSO_4$, filtered and reconcentrated. Kugelrohr distillation of the residue and redistillation at 132−135 °C at 0.05 Torr afforded 14.02 g (86.5%) of TLC- and GC-pure L12b as a colorless oil; $R_f = 0.45$ using 5:95 ethyl acetate/hexane. $^{13}$C-NMR (100.6 MHz, $CDCl_3$), $\delta$ in ppm (carbon environment): 15.44 ($CH_3$), 28.68, 30.86, 32.20, 32.94 (all $CH_2$). FT-IR (KBr), $\bar{\nu}$ in cm$^{-1}$ (relative intensity): 2945(m), 2916(s), 2847(m), 1427(s), 1342(w), 1300(w), 1258(m), 1180(m), 1124(w), 1019(w), 954(w), 772(w), 731(w). EI-MS, *m/z* (relative intensity): 270 $M^+$(12), 148(18), 121(66), 93(21), 73(39), 61(100).

**1,2-Bis[(3-(methylthio)propyl)thio]benzene (bz-$Me_2$-3,2,3-$S_4$ = L13).** In similar fashion to the preparation of L12b, the washed residue from condensation of 1,2-bis[(3-(chloropropyl)thio]benzene, 5.90 g (0.02 mol), with 2 equiv of sodium methanethiolate showed by TLC analysis a minor ($R_f = 0.58$) and a major ($R_f = 0.35$) component using 5:95 ethyl acetate/hexane. The minor component was subsequently characterized as 2,3-benzo-1,4-dithiacycloheptane and separated as solid sublimate below 80 °C at 0.05 Torr during Kugelrohr distillation. The L13 compound was isolated as a colorless oil, 5.2 g (82%), from two Kugelrohr distillations; bp = 165−168 °C at 0.02 Torr. The desired compound was isolated as a colorless oil; $R_f = 0.45$ using 5:95 ethyl acetate/hexane. $^{13}$C-NMR (100.6 MHz, $CDCl_3$), $\delta$ in ppm (carbon environment): 15.40 ($CH_3$), 28.05, 31.95, 33.03 (all $CH_2$), 126.28 (CH), 128.98 (CH), 136.80 (C). FT-IR (KBr), $\bar{\nu}$ in cm$^{-1}$ (relative intensity): 3051(w), 2970(m), 2915(s), 2847(w), 1540(m), 1440(s), 1401(s), 1250(s), 1039(m), 744(s). EI-MS, *m/z* (relative intensity): 318 $M^+$(100), 304(18), 153(48), 89(52), 61(72).

***trans*-1,2-Bis[(3-(methylthio)propyl)thio]cyclohexane (*trans*-cyhx-$Me_2$-3,2,3-$S_4$ = L15).** In similar fashion to the preparation of L13, the washed residue from the condensation of *trans*-1,2-bis((3-chloropropyl)thio)cyclohexane, 9.03 g (0.03 mol), with 2 equiv of sodium methanethiolate showed by TLC analysis a nearly pure major component, $R_f = 0.45$, using 5:95 ethyl acetate/hexane. Kugelrohr distillation and redistillation afforded 6.08 g (62.6%) of L15 as a pale yellow oil, bp = 181−185 °C at 0.03 Torr. $^{13}$C-NMR (100.6 MHz, $CDCl_3$), $\delta$ in ppm (carbon environment): 15.50 ($CH_3$), 24.22, 29.11, 30.38, 31.88, 33.25 (all $CH_2$), 48.79 (CH). FT-IR (KBr), $\bar{\nu}$ in cm$^{-1}$ (relative intensity): 2932(s), 2854(m), 1440(m), 1300(w), 1257(m), 1201(w), 1005(w), 954(w), 835(w), 715(w). EI-MS, *m/z* (relative intensity): 324 $M^+$(4), 121(100), 73(15), 61(18), 59(5).

***cis*-1,2-Bis[(3-(methylthio)propyl)thio]cyclohexane (*cis*-cyhx-$Me_2$-3,2,3-$S_4$ = L14).** In similar fashion to the preparation of L13, the washed residue from the condensation of *cis*-1,2-bis[(3-(chloropropyl)-thio]cyclohexane, 6.02 g (0.02 mol), with 2 equiv of sodium methanethiolate showed by TLC analysis a trace component at $R_f = 0.45$ and the major component at $R_f = 0.40$ using 5:95 ethyl acetate/hexane. Kugelrohr distillation, followed by two redistillations, afforded 5.14 g (79.3%) of L14 as a pale yellow oil, bp = 160−164 °C at 0.03 Torr. TLC analysis still showed traces of the minor component at $R_f = 0.45$. NMR analysis confirmed this to be L15, present at less than 0.5% of L14, due to contamination of the initial *cis*-cyclohexanedithiol by the *trans* isomer at the beginning of the reaction scheme. The *cis* derivative containing the trace of the *trans* derivative was used without further purification for the thermodynamic and kinetic studies. $^{13}$C-NMR (100.6 MHz, $CDCl_3$), $\delta$ in ppm (carbon environment): 15.49 ($CH_3$), 23.44, 30.91, 31.49 33.16 (all $CH_2$), 49.68 (CH). FT-IR (KBr), $\bar{\nu}$ in cm$^{-1}$ (relative intensity): 2932(s), 2854(m), 1440(m), 1343(w), 1292(w), 1202(w), 1155(m), 1125(w), 991(w), 920(w), 835(w), 752(w), 694(w). EI-MS, *m/z* (relative intensity): 324 $M^+$(11), 121(100), 73(20), 61(64), 59(62).

**Other Reagents and Instrumentation.** Procedures for the preparation of all counter reagents utilized in this work have been previously described.[7,8] The preparation of $Cu(ClO_4)_2$ and $Hg(ClO_4)_2$ by the reaction of $HClO_4$ with the appropriate oxides or carbonates and standardization of their solutions have also been previously described.[21] Due to their low solubility, the ligands were dissolved in solutions containing a large excess of hexaaquacopper(II) to prepare the $Cu^{II}L$ solutions for further study. Ligand concentrations of solutions utilized for stability constant measurements were determined by potentiometric titrations against standard Hg(II) solutions using a Reilley mercury pool indicating electrode. The concentrations of $Cu^{II}L$ solutions were determined by spectrophotometric absorbance measurements. Absorbance data for the stability constant determinations were obtained using a Cary 17D double-beam recording spectrophotometer equipped with a thermostated cell compartment. Kinetic data were obtained using a thermostated Durrum Model D-110 stopped-flow spectrophotometer which was interfaced to an Eltech Turbo XT microcomputer with a Metrabyte 12 bit A/D board.

## Results

**Stability Constants for Cu(II) Complexes.** The stability constant for $Cu^{II}$(L12a) has been previously reported (Table 1).[22] No complex was observed to form between Cu(II) and L13 in aqueous solution and this ligand system was not studied further. Stability constant values for the Cu(II) complexes formed with L12b, L14, and L15 were determined at 25 °C from spectrophotometric absorbance data using the method of McConnell and Davidson[23] as previously described.[22] In all three cases, the ionic strength was maintained at 0.10 M using $NaClO_4$. We

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have noted in earlier studies on related tetrathiaether ligands that the perchlorate ion shows evidence of forming an adduct with the Cu(II)−tetrathiaether complexes[22,24] (which does not affect the visible absorption bands) so that "conditional" constants, $K_{\mathrm{Cu^{II}L'}}$,

$$K_{\mathrm{Cu^{II}L'}} = \frac{[\mathrm{Cu^{II}L'}]}{[\mathrm{Cu_{aq}}^{2+}][\mathrm{L}]} \tag{2}$$

are reported where $[\mathrm{Cu_{aq}}^{2+}]$ and [L] represent the equilibrium concentrations of uncomplexed hexaaquacopper(II) ion and ligand, respectively, and $[\mathrm{Cu^{II}L'}]$ is defined as[22]

$$[\mathrm{Cu^{II}L'}] = [\mathrm{CuL}^{2+}] + [\mathrm{CuL(ClO_4)}^{+}] \tag{3}$$

The resulting $K_{\mathrm{Cu^{II}L'}}$ values are tabulated in Table 1 where they are compared to the value for the Cu(II) complex with the corresponding macrocyclic ligand, [14]aneS$_4$.

**Redox Potentials.** The aqueous redox potential for Cu$^{\mathrm{II/I}}$(L12a) had been determined previously by slow-scan cyclic voltammetry (CV)[25] and by stepwise potentiostatic measurements[26] with slightly differing results. The potential for this system was re-determined along with those for the other acyclic systems using the slow-scan CV approach:

$$\mathrm{Cu^{II}L'} + \mathrm{e^-} \rightleftharpoons \mathrm{Cu^{I}L'} \qquad E_{1/2} \tag{4}$$

To ensure that dissociation of the Cu$^{\mathrm{II}}$L′ species was kept to a minimum, the concentration of Cu(ClO$_4$)$_2$ was maintained at very high levels: 0.10 M for both L12a and L12b ($\mu$ = 0.30) and 0.033 M ($\mu$ = 0.10) for the other two acyclic systems. In all cases, the voltammograms appeared to be reversible for sweep rates ranging from 25 to 1000 mV s$^{-1}$ and the half-wave potentials did not vary. Therefore, the latter values are assumed to approximate the formal potentials (Table 1). It should be noted that the new $E^{\mathrm{f}}$ value for Cu$^{\mathrm{II/I}}$(L12a) is in virtual agreement with that obtained previously with the potentiostatic method,[26] suggesting that the original CV measurement[25] (in which a smaller excess of Cu(II) was used) was affected by Cu$^{\mathrm{II}}$L dissociation.

**Stability Constants for Cu(I) Complexes.** The apparent stability constants for the Cu$^{\mathrm{I}}$L complexes, $K_{\mathrm{Cu^{I}L'}}$, were calculated from the Nernst equation by utilizing the formal potentials and the conditional stability constants for the corresponding Cu$^{\mathrm{II}}$L′ species, $K_{\mathrm{Cu^{II}L'}}$:[26]

$$E_{\mathrm{Cu^{II/I}L}}{}^{\mathrm{f}} = E_{\mathrm{Cu(II/I)_{aq}}}{}^{\mathrm{f}} - \frac{2.303RT}{F}\log\frac{K_{\mathrm{Cu^{II}L'}}}{K_{\mathrm{Cu^{I}L'}}} \tag{5}$$

In eq 5, $E_{\mathrm{Cu(II/I)_{aq}}}{}^{\mathrm{f}}$ represents the formal potential of the aquated Cu(II/I) redox couple for which a value of 0.13 V (vs NHE) was utilized.[27] The resultant $K_{\mathrm{Cu^{I}L'}}$ values are included in Table 1.

**Table 2.** Redox Potentials, Self-Exchange Rate Constants, and Effective Contact Radii for Counter Reagents Utilized in This Work, Where Values Shown Are for Aqueous Solution at 25 °C, $\mu$ = 0.10 M

| counter reagent | $E^{\mathrm{f}}$, V vs NHE | $k_{22}$, M$^{-1}$ s$^{-1}$ | $10^8r$, cm |
|---|---|---|---|
| | Reductants | | |
| Co$^{\mathrm{II}}$(phen)$_3$ | 0.42$^{a}$ | 40$^{a}$ | 7.0$^{a}$ |
| Co$^{\mathrm{II}}$(bpy)$_3$ | 0.32$^{b}$ | 17$^{a,b}$ | 7.0$^{a}$ |
| Ru$^{\mathrm{II}}$(NH$_3$)$_4$bpy | 0.526$^{c}$ | $2.2 \times 10^{6\ d}$ | 4.4$^{e}$ |
| Ru$^{\mathrm{II}}$(NH$_3$)$_5$isn | 0.387$^{f}$ | $1.1 \times 10^{5\ g}$ | 3.8$^{g}$ |
| Ru$^{\mathrm{II}}$(NH$_3$)$_5$py | 0.32$^{c}$ | $1.1 \times 10^{5\ d}$ | 3.8$^{d}$ |
| | Oxidants | | |
| Ni$^{\mathrm{III}}$([14]aneN$_4$) | 0.95$^{h,i}$ | $1.0 \times 10^{3\ h,i}$ | 3.6$^{i}$ |
| Ru$^{\mathrm{III}}$(NH$_3$)$_2$(bpy)$_2$ | 0.889$^{j}$ | $8.4 \times 10^{7\ d}$ | 5.6$^{d}$ |
| Fe$^{\mathrm{III}}$(4,7-Me$_2$phen)$_3$ | 0.939$^{e}$ | $3.3 \times 10^{8\ k}$ | 6.6$^{e}$ |

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**Electron-Transfer Cross Reaction Rate Constants**. All Cu(II/I)−polythiaether systems exhibit relatively high redox potentials so that the Cu$^{\mathrm{I}}$L complexes are readily accessible for study.[25,26,28] For the acyclic polythiaethers, however, the Cu$^{\mathrm{II}}$L complexes are very weak ($K_{\mathrm{Cu^{II}L}} = 10^1{-}10^3$ M$^{-1}$) making it necessary to study the Cu$^{\mathrm{II}}$L reduction kinetics in the presence of very large excesses of aquacopper(II) ion. Aside from being an inconvenience, the presence of high concentrations of solvated Cu(II) should not present a significant kinetic problem in aqueous solution since Sisley and Jordan have shown that the self-exchange rate constant for Cu(II/I)$_{\mathrm{aq}}$ is extremely small ($\approx 10^{-7}$ M$^{-1}$ s$^{-1}$)[29] in the absence of inner-sphere bridging species.

The oxidation kinetics for each Cu$^{\mathrm{I}}$L complex were studied with three different counter reagents: Ni$^{\mathrm{III}}$([14]aneN$_4$), Ru$^{\mathrm{III}}$(NH$_3$)$_2$bpy$_2$, and Fe$^{\mathrm{III}}$(4,7-Me$_2$phen)$_3$.[30] Reduction kinetics of the Cu$^{\mathrm{II}}$L complexes were also studied using at least three reagents: Co$^{\mathrm{II}}$(bpy)$_3$, Ru$^{\mathrm{II}}$(NH$_3$)$_4$bpy, and Ru$^{\mathrm{II}}$(NH$_3$)$_5$isn.[30] For the reduction of Cu$^{\mathrm{II}}$(L12a) and Cu$^{\mathrm{II}}$(L12b), Ru$^{\mathrm{II}}$(NH$_3$)$_5$py or Co$^{\mathrm{II}}$(phen)$_3$, respectively, was utilized as a fourth reducing agent. The potentials, self-exchange rate constants, and estimated ion size parameters used for all eight reagents are provided in Table 2.

For all cases, reaction 1 was found to be first order with respect to each reactant, indicating the absence of conformational gating. Most kinetic measurements were carried out under conditions in which the two reactant concentrations were initially within the same order of magnitude and the reaction kinetics were analyzed using the standard integrated form of the second-order expression. For the slower reactions involving nickel and cobalt reagents, pseudo-first-order conditions were utilized in which the counter reagent was present in large excess over the

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(30) Ligand abbreviations are as follows: [14]aneN$_4$ = 1,4,8,11-tetraazacyclotetradecane; bpy = 2,2′-bipyridine; 4,7-Me$_2$phen = 4,7-dimethyl-1,10-phenanthroline; isn = isonicotinamide; phen = 1,10-phenanthroline; py = pyridine.

**Table 3.** Second-Order Electron-Transfer Rate Constants for the Reactions of Copper (II/I)−Acyclic Tetrathiaether Complexes with Selected Counter Reagents in Aqueous Solution at 25 °C, $\mu = 0.10$ M (Except As Noted)

| | $k_{12}$ (or $k_{21}$), $M^{-1}\,s^{-1}$ | | | |
|---|---|---|---|---|
| counter reagent | $Me_2$-2,3,2-$S_4$ (L12a) | $Me_2$-3,2,3-$S_4$ (L12b) | *cis*-cyhx-$Me_2$-3,2,3-$S_4$ (L14) | *trans*-cyhx-$Me_2$-3,2,3-$S_4$ (L15) |
| | | Reductants | | |
| $Co^{II}(phen)_3$ | | $2.2(2) \times 10^4$ [a] | | |
| $Co^{II}(bpy)_3$ | $1.9(1) \times 10^5$ [a] | $5.4(4) \times 10^4$ [a] | $5.1(4) \times 10^4$ | $3.64(6) \times 10^4$ |
| $Ru^{II}(NH_3)_4bpy$ | $5.1(4) \times 10^5$ [a] | $1.4(2) \times 10^6$ [a] | $3.2(4) \times 10^5$ | $4.3(2) \times 10^5$ |
| $Ru^{II}(NH_3)_5isn$ | $[1.9(3), 3.0(6), 4(1)] \times 10^6$ [a,b] | $2.3(5) \times 10^6$ [a] | $7.9(8) \times 10^5$ | $1.1(2) \times 10^6$ |
| $Ru^{II}(NH_3)_5py$ | $2.5(8) \times 10^6$ [a] | | | |
| | | Oxidants | | |
| $Ni^{III}([14]aneN_4)$ | $5.7(1) \times 10^2$ | $6.12(1) \times 10^3$ | $1.00(2) \times 10^4$ | $5.8(1) \times 10^3$ |
| $Ru^{III}(NH_3)_2(bpy)$ | $4.0(4) \times 10^4$ | $3.2(1) \times 10^5$ | $4.0(9) \times 10^5$ | $2.6(2) \times 10^5$ |
| $Fe^{III}(4,7\text{-}Me_2phen)_3$ | $[8(1), 8.5(8)] \times 10^5$ [b,c] | $1.5(3) \times 10^6$ | $2.5(8) \times 10^6$ | $1.6(1) \times 10^6$ |

[a] $\mu = 0.20$ M. [b] Results shown are from multiple studies. [c] Previously reported value is $k_{21} = 4.7 \times 10^4\ M^{-1}\,s^{-1}$ (corrected for revised potential for $Cu^{II/I}(Me_2\text{-}2,3,2\text{-}S_4)$, $E^f = 0.79$ V)—see ref 2.

**Table 4.** Calculated Logarithmic Electron Self-Exchange Rate Constants for the Copper(II/I)−Acyclic Tetrathiaether Complexes at 25 °C, $\mu = 0.10$ M ($ClO_4^-$) (Except As Noted)

| | log $k_{11}$ ($M^{-1}\,s^{-1}$) | | | |
|---|---|---|---|---|
| counter reagent | $Me_2$-2,3,2-$S_4$ (L12a) | $Me_2$-3,2,3-$S_4$ (L12b) | *cis*-cyhx-$Me_2$-3,2,3-$S_4$ (L14) | *trans*-cyhx-$Me_2$-3,2,3-$S_4$ (L15) |
| | | Reductants | | |
| $Co^{II}(phen)_3$ | | 0.77 [a] | | |
| $Co^{II}(bpy)_3$ | 2.3 [a] | $1.2_5$ [a] | $1.5_8$ | 1.01 |
| $Ru^{II}(NH_3)_4bpy$ | 0.8[a] | $1.2_4$[a] | 0.96 | 0.93 |
| $Ru^{II}(NH_3)_5isn$ | 1.3, 1.7, 2.0[a,b] | 0.75[a] | 0.97 | 1.04 |
| $Ru^{II}(NH_3)_5py$ | 0.7 [a] | | | |
| | | Oxidants | | |
| $Ni^{III}([14]aneN_4)$ | −0.4 | $2.3_3$ | $1.5_0$ | $1.3_2$ |
| $Ru^{III}(NH_3)_2(bpy)_2$ | −0.4 | 2.07 | 1.04 | 0.80 |
| $Fe^{III}(4,7\text{-}Me_2phen)_3$ | 0.9, 0.9[b,c] | 2.04 | $1.3_1$ | $1.2_2$ |

[a] $\mu = 0.20$ M. [b] Results shown are from multiple studies. [c] Previously reported value is log $k_{11} = -1.6$ (corrected for revised $Cu^{II/I}(Me_2\text{-}2,3,2\text{-}S_4)$, $E^f = 0.79$ V)—see ref 2.

copper complex concentration. The initial $Cu^{II}$(L12a) and $Cu^{II}$(L12b) solutions contained 0.10 M excess aquacopper(II) ion which was reduced to 0.05 M upon mixing. Dependent upon the relative rates of $Cu^{II}$(L12b) dissociation and oxidation, this implies that 40−57% of the ligand remains uncomplexed at the start of the reaction. Since there was concern that uncomplexed ligand could react with the excess copper to form additional $Cu^{II}L$ as reduction takes place, the kinetic data were analyzed using varying initial reaction segments. Consistent rate constants were obtained for at least the first 40% of the reaction. The mean values of the resolved second-order cross reaction rate constants for all reactions are summarized in Table 3.

## Discussion

**Calculation of Self-Exchange Rate Constants.** For each electron-transfer reaction studied (reaction 1), the $Cu^{II/I}L$ self-exchange rate constant, $k_{11}$, was calculated from the experimentally determined cross-reaction rate constant using the Marcus relationship:[10]

$$k_{11} = \frac{(k_{12})^2}{k_{22}K_{12}f_{12}(W_{12})^2} \tag{6}$$

In eq 6, $k_{22}$ is the self-exchange rate constant for the counter-reagent (Table 1), $K_{12}$ is the equilibrium constant for the cross reaction as calculated from the formal potentials of the two reactants, $f_{12}$ represents a nonlinear correction term,[2] and $W_{12}$ represents a correction for the electrostatic work term involved in bringing the two reactants into proximity for reaction (as previously described).[2] No attempt was made to correct potentials or equilibrium constants for the differences in ionic strength for the reduction studies on $Cu^{II}$(L12a) and $Cu^{II}$(L12b) since such corrections are insignificant relative to the inherent experimental errors incurred with these weak complexes. The $k_{11}$ values calculated using eq 6 are tabulated in Table 4 for all reactions studied.

The $k_{11}$ values obtained for $Cu^{II/I}$(L12a) are worthy of special comment. In our original survey,[2] we reported a value of log $k_{11(Red)} = 5.9$ (corrected for $E^f = 0.79$ V for $Cu^{II/I}$(L12a)—see Table 1) based on the reduction of $Cu^{II}$(L12a) with $Co^{II}(Me_4\text{-}[14]tetraeneN_4)$.[31] Since the latter reagent has solvated apical sites which could conceivably be involved in inner-sphere bridging (via hydroxide) to a solvated inner-sphere site on $Cu^{II}L$, studies with that specific reagent were not repeated in the current work. However, the use of three different Ru(II) reducing agents have yielded values of log $k_{11(Red)}$ ranging from 0.7 to about 1.7 (Table 4) which we assume to be reasonably reliable. (A higher value obtained with $Co^{II}(bpy)_3$ is considered less reliable since the excess Cu(II) present in solution might extract bpy from Co(II).) On the basis of these new and more extensive results, we conclude that the originally reported $k_{11(Red)}$ value for $Cu^{II}$(L12a) was too large by 4−5 orders of magnitude. It is possible that the earlier result involved an inner-sphere mechanism as suggested above, but the source of error cannot be definitively assigned.

For the oxidation of $Cu^{I}$(L12a) with $Fe^{III}(4,7\text{-}Me_2phen)_3$, we originally obtained log $k_{11(Ox)} = -1.6$ (corrected for $E^f = 0.79$ V) whereas the corresponding value in the current work is 0.9, a value which has been duplicated in two successive series of measurements. Although we are uncertain of the source of apparent error in the original study, we note that, in our initial

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(31) $Co^{II}(Me_4[14]tetraeneN_4)(H_2O)_2$ represents the diaquo(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)cobalt(II) ion: Durham, B. Ph.D. Dissertation, Wayne State University, 1977.

survey,[2] several different $k_{11(\mathrm{Ox})}$ values were obtained for the $\mathrm{Cu^I(Et_2\text{-}2,3,2\text{-}S_4)}$ complex reacting with $\mathrm{Fe^{III}(4,7\text{-}Me_2phen)_3}$ and $\mathrm{Fe^{III}(bpy)_3}$ which suggests the existence of some experimental difficulties or, possibly, the onset of the conformationally gated region. In the current work on $\mathrm{Cu^{II/I}}$(L12a), the values calculated for $k_{11(\mathrm{Ox})}$ with various reagents is somewhat inconsistent. It is unclear whether these disagreements are due to problems with $\mathrm{Cu^IL}$ solubility limitations or some other experimental error. Nonetheless, taken as a whole, the current data for $\mathrm{Cu^{II/I}}$(L12a) indicate that $k_{11(\mathrm{Red})}$ and $k_{11(\mathrm{Ox})}$ are of similar magnitude, in dramatic contrast to our original study in which these self-exchange rate constants differed by $10^7$.

The $k_{11(\mathrm{Red})}$ and $k_{11(\mathrm{Ox})}$ values for the $\mathrm{Cu^{II/I}}$(L12b) system are each internally consistent but differ by about 1 order of magnitude. This difference is presumed to originate from the experimental difficulties associated with the instability of the $\mathrm{Cu^{II}}$(L12b) complex. In recognition of this fact, the level of consistency of all $k_{11}$ values for this system is considered to be within tolerable limits. The $k_{11}$ values for the much more stable L14 and L15 systems are clearly within the limits of experimental reproducibility for all reactions studied.

**Comparison to Copper(II/I)−Macrocyclic Tetrathiaether Systems.** The kinetic behavior of the acyclic tetrathiaether complexes contrasts sharply with the $k_{11}$ trends which we have previously observed for the corresponding Cu(II/I) systems with the macrocycles [13]ane$\mathrm{S_4}$,[6] [14]ane$\mathrm{S_4}$,[4] [15]ane$\mathrm{S_4}$,[6] and derivatives thereof.[7,32] In those cases, the $k_{11}$ values calculated from *rapid* $\mathrm{Cu^IL}$ oxidation reactions were smaller than the corresponding values evaluated from $\mathrm{Cu^{II}L}$ reduction reactions by 2−5 orders of magnitude. As noted in the Introduction, such a pattern of $k_{11}$ values reflects the existence of a dual-pathway square scheme (Scheme 1) in which, under appropriate conditions, the conformational change $\mathrm{Cu^IL(R)} \rightarrow \mathrm{Cu^IL(P)}$ becomes rate-limiting and eventually brings about a switch in the preferred reaction pathway. In several of the macrocyclic systems, in fact, it was possible to demonstrate the specific onset of first-order behavior in the oxidation, indicative of such conformational gating.

Even if all calculated $k_{11(\mathrm{Red})}$ and $k_{11(\mathrm{Ox})}$ values for the $\mathrm{Cu^{II/I}}$(L12a) system were deemed to be accurate, the patterns for the acyclic tetrathiaether systems do not fit those to be expected for a dual-pathway square scheme mechanism. In fact, for all of the complexes included in the current work, there is no clear trend in the $k_{11}$ values determined from reduction and oxidation reactions. Therefore, we conclude that there is no clear evidence that multiple reaction pathways exist.

The observation that each specific system is proceeding by a single pathway leads to the conclusion that, within the conditions sampled in this study, the conformational changes accompanying electron-transfer for the Cu(II/I)−acyclic tetrathiaether complexes are rapid relative to the overall kinetic behavior. This is consistent with the flexible nature of the acyclic species.

**Comparison to Other Copper(II/I)−Acyclic Ligand Systems.** Stanbury, Wilson, and co-workers have reported similar cases of Cu(II/I) systems in which constant $k_{11}$ values were observed for both oxidation and reduction.[33−35] Their systems involve acyclic ligands containing five unsaturated nitrogen donor atoms in which the copper ion tends to maintain relatively uniform five-coordinate geometries in both oxidation states. Therefore, they have ascribed the consistency of the self-exchange rate constant behavior for oxidation and reduction to the coordination invariance of the central metal ion. The current work illustrates the fact that coordination invariance is not a required condition for exhibiting single-pathway behavior.

Unfortunately, there are no other Cu(II/I) complexes involving linear acyclic ligands for which both $\mathrm{Cu^{II}L}$ reduction and $\mathrm{Cu^IL}$ oxidation kinetic data are available for comparison to the current systems. The only closely related copper complex for which extensive kinetic data have been reported is that involving pdto (Figure 1), a dithiaether ligand with terminal pyridine groups. This ligand is closely related to $\mathrm{Me_2\text{-}3,2,3\text{-}S_4}$ but is more amenable to study due to the much greater stability of the Cu(II) complex. Moreover, the coordination geometries of its Cu(II) and Cu(I) complexes have been determined[36] and are similar to those presumed to exist for the corresponding complexes in the current study. Although no oxidation studies have been reported to date, reductions of $\mathrm{Cu^{II}}$(pdto) with five different reagents have yielded calculated log $k_{11(\mathrm{Red})}$ values ranging from 0.7 to 1.6,[37,38] in the same range as the values found for our current acyclic tetrathiaether systems. This similarity is significant since the terminal pyridine nitrogens are more likely to remain coordinated throughout the reaction than are the terminal sulfurs in our complexes. Thus, the lability of the terminal sulfurs in our acyclic systems would not appear to be a major factor in governing the electron-transfer kinetics. A single reduction study on $\mathrm{Cu^{II}}$(3dta), where 3dta represents an analogue of L12a in which the terminal thiaethers have been replaced by labile carboxylates, has yielded a similar log $k_{11(\mathrm{Red})}$ value of 1.6.[39]

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