conversion rate of the mono-G-N7-substituted intermediates to the A-N7–G-N7 adducts. That is, it is the equivalent of k_3 in the symmetric case. Quite accurate data were obtained, and as can be seen in Table III, the value of k_{av} obtained for cisplatin is about the same for Pt(mma), Pt(mma)$_2$, Pt(mea)$_2$, Pt(mea), and Pt(en) and shows good agreement with the cisplatin data obtained by Chottard et al.[13b] The only exceptions are the asymmetric Pt(dma) and the Pt(dma)$_2$ and Pt(dea)$_2$ compounds, which show a remarkable decrease in their second-step velocity. The decrease factor is about 2 for asymmetric Pt(dma), about 10 for Pt(dma)$_2$, and even about 300 for the bulky Pt(dea)$_2$.

In the case of the asymmetric compound an interesting pattern in the comparison of k_3 and k_4 is observed. Although the value for k_{av} does not change for Pt(mma) and Pt(mea), there is no equality for k_3 and k_4. In the case of Pt(mma), k_3 is 1.5 times larger than k_4, and in the case of Pt(dma) and Pt(mea), k_3 is about 2.5 times k_4. The difference of the second step becomes clear by comparing k_3 and k_4. The alkyl substitution begins to become remarkably effective in the second step of the reaction.

One would expect that the rotation around the Pt–G-N7 bond, directing the second binding place of the *cis*-platinum amine complex toward A-N7, is an important step in the second-step reaction,[9,10] which would lead to a small value of k_3 (corresponding to the conversion rate from the intermediate **1**, which has the alkyl amino group cis to the guanine residue). However, as can be seen in Table III, the value for k_3 is larger than for k_4 in all cases. Therefore, rotation around the Pt–G-N7 bond does not appear to play an important role in the kinetics of the chelation step.

It was already pointed out that although k_4 decreases, k_{av} does not decrease in the case of Pt(mma) and Pt(mea). The increase in the value of k_3 might originate from an instability of its monofunctional intermediate. As a result, the conversion to the adduct **1** might become easier.

Concluding Remarks

The reaction of substituted cisplatin analogues with r(ApG) results in one or two A-N7–G-N7 adducts as the major product, depending upon the symmetry of the platinum compound. The resulting structures seem to deviate slightly from cisplatin, as deduced from NMR and CD data. On the other hand, the

substituents appear to have a marked influence on the reaction velocity of both the first binding step and the chelation step. Especially in the case of secondary amine derivatives, slow kinetics are observed.

The recently published results of Arpalahti and Lippert[13a] about the kinetics of cisplatin derivatives in reaction with nucleosides is in good agreement with our results. They found that the order of reactivity is RNH$_2$ ≥ NH$_3$ > R$_2$NH, whereas we found NH$_3$ > RNH$_2$; this small deviation is easily understood from the fact that they use mononucleotides (for which hydrogen bonding is not so important), whereas in our case the phosphate group is likely to have the most important interaction[30] with NH$_3$.

It should be taken into account that for example [Pt(dien)Cl]Cl, a monofunctionally binding compound often used for mimicking the intermediate of a reaction between cisplatin and a nucleic acid,[31] is not antitumor active.[32] Therefore, also a substituted cisplatin analogue with a very slow chelation step may not exhibit any antitumor activity. Perhaps the low antitumor activity of cisplatin analogues containing bulky nonleaving groups is related to the slow kinetics. Preliminary time-dependent cytotoxicity experiments[16] seem to corroborate this hypothesis.

(31) van Garderen, C. J.; van Houte, L. P. A.; van den Elst, H.; van Boom, J. H.; Reedijk, J. *J. Am. Chem. Soc.* **1989**, *111*, 4123.
(32) Pinto, A. L.; Lippard, S. J. *Proc. Natl. Acad. Sci. U.S.A.* **1985**, *82*, 4616.

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Electrochemical Properties of Copper(II)/Copper(I)–Macrocyclic Polythia Ether Complexes: Determination of Formal Potential Values and Cyclic Voltammetric Behavior

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Extensive potentiostatic and cyclic voltammetric studies have been carried out on a series of copper–polythia ether complexes, including macrocyclic and acyclic ligand species, in both aqueous and 80% methanol (w/w) solutions. From the accumulated data, a recommended set of formal potential values are reported for the Cu$^{II/I}$L redox couples in aqueous solution at 25 °C. On the basis of these potentials and previously measured stability constants for the Cu^{II}L species, the apparent stability constants for the Cu^{I}L species have been calculated. The formal potential values and Cu^{I}L stability constants in aqueous solution are as follows (for 25 °C, 0.10 M ClO$_4^-$, listed in the following order: complexed ligand, E^f in V vs SHE, log $K_{Cu^I L}$): [12]aneS$_4$, <0.69 V, <12.$_8$; [13]aneS$_4$, ≈0.52 V, ≈10.0; [14]aneS$_4$, 0.59 V, 12.1$_1$; *syn*-[14]aneS$_4$-diol, 0.52 V, 9.7$_1$; [15]aneS$_4$, 0.64 V, 11.7$_9$; [16]aneS$_4$, 0.71 V, 12.0$_0$; [15]aneS$_5$, 0.69 V, 13.6$_5$; Me$_2$-2,3,2-S$_4$, ≈0.79 V, ≈13.1; Et$_2$-2,3,2-S$_4$, 0.79 V, 13.3$_4$. Anomalous cyclic voltammetric behavior was observed for the [12]aneS$_4$ system, which appears to be consistent with the previously proposed "square scheme" mechanism involving metastable intermediates of both the Cu^{I}L and Cu^{II}L species.
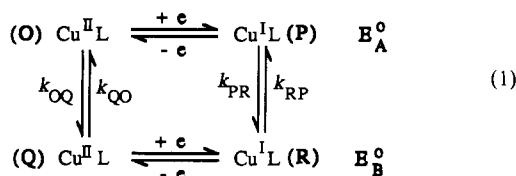
Introduction

Recently, we have reported the results of both homogeneous[1] and heterogeneous[2] electron-transfer studies involving low mo-

lecular weight copper–polythia ether complexes that appear to support the existence of a "square scheme" mechanism.

(1) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012–3022.
(2) Bernardo, M. M.; Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1224–1231.

$$
\begin{array}{cc}
\text{(O)} \ \text{Cu}^{II}\text{L} & \underset{-\,e}{\overset{+\,e}{\rightleftharpoons}} \ \text{Cu}^{I}\text{L} \ \text{(P)} \qquad E_A^o \\
k_{OQ} \updownarrow k_{QO} & k_{PR} \updownarrow k_{RP} \\
\text{(Q)} \ \text{Cu}^{II}\text{L} & \underset{-\,e}{\overset{+\,e}{\rightleftharpoons}} \ \text{Cu}^{I}\text{L} \ \text{(R)} \qquad E_B^o
\end{array}
\tag{1}
$$

In this scheme, species O and R represent the thermodynamically stable conformers of Cu^{II}L and Cu^{I}L, respectively, and Q and P represent metastable intermediates. This mechanism yields two competing mechanistic pathways for electron transfer, O $\rightleftharpoons$ P $\rightleftharpoons$ R and O $\rightleftharpoons$ Q $\rightleftharpoons$ R, which are controlled by the rate constants for conformational interconversion (k_{OQ}, k_{QO}, k_{PR}, k_{RP}). Such square scheme mechanisms are of particular interest since they are believed to serve as the basis for gated electron-transfer behavior in biological systems and have recently been described in theoretical terms by Hoffman and Ratner[3] and by Brunschwig and Sutin.[4]

The presence of the metastable intermediates has been shown to generate unusual electrochemical behavior when utilizing temporal methods, such as cyclic voltammetry (CV), under conditions where the duration of the potential scan occurs within the time domain of the mean lifetimes associated with the conformational changes.[2] Whereas this time-dependent behavior is useful in characterizing the overall square scheme, its appearance has caused us to reexamine the thermodynamic data previously reported for the overall electron-transfer processes to insure that the previously reported data were not influenced by the kinetic characteristics of the square scheme itself.

In the current paper, we describe the results of careful static and dynamic measurements designed to determine accurately the formal electrochemical potentials for the redox processes represented by the general half-reaction

$$
\text{Cu}^{II}\text{L}' + \text{e}^- \rightleftharpoons \text{Cu}^{I}\text{L}' \qquad E^f
\tag{2}
$$
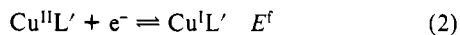
In the course of making these measurements, we have also attempted to characterize the major factors affecting the electrochemical behavior of this series of compounds under normal solution conditions and at relatively slow sweep rates. In this process, we have discovered an additional system that exhibits behavior characteristic of conformational control in its cyclic voltammetric behavior.

The copper complexes described in this work involve six macrocyclic and two acyclic tetrathia ethers plus a macrocyclic pentathia ether, viz.: 1,4,7,10-tetrathiacyclododecane ([12]aneS$_4$); 1,4,7,10-tetrathiacyclotridecane ([13]aneS$_4$); 1,4,8,11-tetrathiacyclotetradecane ([14]aneS$_4$); 1,4,8,12-tetrathiacyclopentadecane ([15]aneS$_4$); 1,5,9,13-tetrathiacyclohexadecane ([16]aneS$_4$); 3,6,10,13-tetrathiacyclotetradecane-1,8-diol ([14]aneS$_4$-diol); 2,5,9,12-tetrathiatridecane (Me$_2$-2,3,2-S$_4$); 3,6,10,13-tetrathiapentadecane (Et$_2$-2,3,2-S$_4$); and 1,4,7,10,13-pentathiacyclopentadecane ([15]aneS$_5$). A portion of the data on three of these systems ([14]aneS$_4$, [14]aneS$_4$-diol, and [15]aneS$_4$), focusing on a characterization of the square scheme based on their cyclic voltammetric behavior at high scan rates and/or very low temperatures, has been reported previously[2] and is not repeated here. All nine ligands are illustrated in Figure 1.

Experimental Section

Instrumental Methods. The experimental procedures used were essentially identical with those described previously[2] and, therefore, are summarized only briefly here. The instrumentation used consisted of a Princeton Applied Research (PAR) Model 175 universal programmer, a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer, a current-to-voltage converter, and an interfaced minicomputer. Reported potentials were measured against the aqueous saturated sodium chloride reference electrode (SSCE, $E^f = 0.247$ V vs SHE) and were not corrected for junction potentials. The auxiliary electrode consisted of a platinum coil. The working electrode consisted of glassy carbon press-
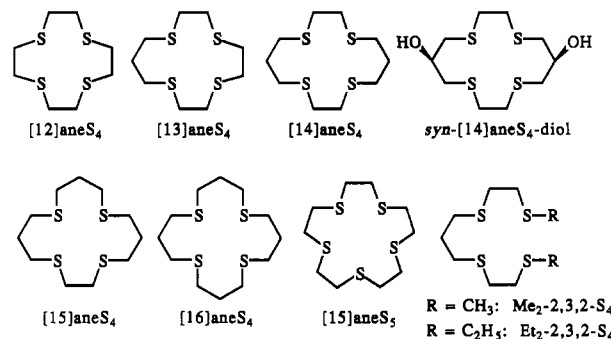

Figure 1. Ligands discussed in this work.

fitted onto a Kel-F shroud (Bioanalytical Systems). Extreme care was taken in the pretreatment of this electrode based on the method recommended by Rusling and co-workers.[5]

For the first peak on any forward scan, the peak current was measured as the absolute difference between the peak current value and the decaying current base line obtained by holding the potential constant at the foot of the peak. The peak current for the first peak on a return scan was corrected by using, as a base line, the current obtained when the potential was held at the switching potential value. In all cases, the base line was obtained by recording the time-dependent current on a second voltammogram when the scan was stopped at the foot of the peak or at the switching potential. Temperature control was maintained by circulating fluid from a temperature bath through a jacket surrounding the covered cell.

Independent potentiostatic measurements of the $E_{1/2}$ values were made by reducing Cu^{II}L solutions in a stepwise fashion while continuously flowing the solution through a spectrophotometric cell inserted into the cell compartment of a Perkin-Elmer Lambda 3B double-beam scanning spectrophotometer equipped with a Model 3600 data station and a Model 660 printer. For these measurements, the potential was held constant until the current decayed to the background level ($\approx$20–30 min) prior to the scan of the UV–visible spectrum. This process was repeated at 20 mV intervals bracketing the approximate formal potential value of the redox species of interest as located by slow-scan cyclic voltammetry. Data collection was extended to include potentials on either side of the E^f value with the total potential range exceeding 250 mV. This process was then reversed and the solution was reoxidized in a similar incremental process.

Reagents. Preparation and purification of Cu(ClO$_4$)$_2$·6H$_2$O and the several polythia ether ligands have been previously described.[6] Copper(II) complex solutions were prepared by dissolving recrystallized copper perchlorate and the macrocyclic ligand in distilled–deionized water or 80% methanol–20% water (prepared by weight using reagent grade methanol from Matheson Coleman and Bell). Due to the limited stability of the Cu^{II}L species, a large excess of Cu(II) ion was added to most solutions to increase the extent to which Cu^{II}L was formed. These solutions were reduced by controlled potential electrolysis to prepare the corresponding Cu^{I}L solutions. Ionic strength was controlled by the addition of reagent grade HClO$_4$ (G. F. Smith Chemical Co.) or NaClO$_4$ salt prepared by the slow addition of HClO$_4$ to reagent grade NaOH, which was then recrystallized twice.

Results

Since the copper–polythia ether complexes have been demonstrated to be totally insensitive to variations in acidity levels below pH $\approx$5.8 (at higher pH levels hydroxocopper(II) species begin to form),[7] most of the studies were conducted in 0.10 M HClO$_4$. For the cyclic voltammetric studies, parallel measurements were frequently carried out in both aqueous solution and in 80% methanol (by weight). The latter solvent generally permitted the use of higher ligand concentrations, due to improved solubility, while being insensitive to small changes in the water content. Moreover, the previously reported CV studies on the Cu$^{II/I}$-([14]aneS$_4$) and Cu$^{II/I}$([14]aneS$_4$-diol) systems indicated that the

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

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

(5) Kamau, G. N.; Willis, W. S.; Rusling, J. F. *Anal. Chem.* **1985**, *57*, 545–551.

(6) Diaddario, L. L.; Zimmer, L. L.; Jones, T. E.; 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.

(7) Pett, V. B.; Leggett, G. H.; Cooper, T. H.; Reed, P. R.; Situmeang, D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1988**, *27*, 2164–2169.

Table I. Formal Potentials (E^f) As Determined for the Copper(II)/Copper(I)-Polythia Ether Complexes by Using Potentiostatic and Cyclic Voltammetric Measurements in Aqueous Solution and in 80% Methanol (by Weight) at 25 °C, 0.10 M HClO$_4$ (All Values in V vs SHE)

| redox couple | potentiostatic measurements aqueous | | cyclic voltammetric measurements | | | | previously reported values | | recommended values aqueous |
| | E^f(redn) | E^f(oxidn) | aqueous | | 80% methanol | | aqueous | 80% MeOH | |
			$E_{1/2}$(Cu^{II}L)	$E_{1/2}$(Cu^{I}L)	$E_{1/2}$(Cu^{II}L)	$E_{1/2}$(Cu^{I}L)	$E_{1/2}{}^a$	$E_{1/2}{}^b$	E^f
Cu$^{II/I}$([12]aneS$_4$)			<0.69^c		0.68		0.64	0.72	<0.69 (0.52?)^c
Cu$^{II/I}$([13]aneS$_4$)			0.52		0.65		0.60	0.67	≈0.52
Cu$^{II/I}$([14]aneS$_4$)	0.578	0.569	0.60	0.61	0.69	0.69	0.60	0.69	0.59
Cu$^{II/I}$([14]aneS$_4$-diol)^d			0.52	0.53	0.55	0.56	0.52^e		0.52
Cu$^{II/I}$([15]aneS$_4$)		0.645	0.63	0.65	0.74	0.74	0.73	0.79	0.64
Cu$^{II/I}$([16]aneS$_4$)	0.719	0.727	0.70	0.70	0.78	0.78	0.77	0.80	0.71
Cu$^{II/I}$([15]aneS$_5$)	0.676	0.671	0.71	0.71	0.82	0.82	0.75	0.86	0.69
Cu$^{II/I}$(Me$_2$-2,3,2-S$_4$)					0.81	0.82	0.82	0.89	≈0.79^f
Cu$^{II/I}$(Et$_2$-2,3,2-S$_4$)	0.786	0.783	0.71^g	0.72^g	0.83	0.83		0.89	0.79

^{a} Reference 12. ^{b} Dockal, E. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4322–4324. ^{c} Value of $E_{1/2}$ obtained under slow scan conditions does not represent an equilibrated condition; value of E^f should be significantly smaller (see text). ^{d} Sample consisted principally of the syn isomer of [14]aneS$_4$-diol; the complex with the anti isomer has $E^f \approx 0.49$ V: Meagher, N. E.; Rorabacher, D. B. Work in Progress. ^{e} Malik, M. M.S. Thesis, Wayne State University: Detroit, MI, 1979. ^{f} Value of E^f for Me$_2$-2,3,2-S$_4$ equated to that for Et$_2$-2,3,2-S$_4$ based on similar behavior in 80% methanol. ^{g} Value of $E_{1/2}$ obtained under slow scan conditions appears to involve adsorption of Cu^{II}L at the electrode surface (see text).

appearance of conformationally controlled electrochemical behavior associated with the square scheme was detectable at slower scan rates and/or higher temperatures in the methanolic media.

Potentiostatic Determination of Formal Potential. Due to the unusual cyclic voltammetric behavior reported previously for the Cu$^{II/I}$([14]aneS$_4$) and Cu$^{II/I}$([14]aneS$_4$-diol) systems, in which multiple peaks were observed to develop as a function of sweep rate and/or temperature,[2] it was concluded that the formal potentials of the various polythia ether complexes should be determined by a method that would insure that equilibrium had been thoroughly established for all measurements. Accordingly, potentiostatic determinations of the E^f values were carried out with spectrophotometric monitoring for the complexes formed with [14]aneS$_4$, [15]aneS$_4$, [16]aneS$_4$, [15]aneS$_5$, and Et$_2$-2,3,2-S$_4$ as outlined in the Experimental Section (the results for the first two systems having been reported previously).[2]

Upon electroreduction of the Cu^{II}L solutions, no shifting of the absorbance bands was detected, but the intensity of the visible bands centered at about 400 and 600 nm [assigned as S(σ) → Cu^{II} charge transfer (≈400 nm)[8] and S(π) → Cu^{II} charge transfer (≈600 nm),[8] the latter possibly mixed with a d–d transition[9]] decreased monotonically while a new shoulder appeared in the UV at about 260 nm, with an isosbestic point in the vicinity of 290 nm (Figure 2). The spectral changes were reversible, and the original spectra were regenerated upon reoxidation of the solutions (with the exception of the [16]aneS$_4$ and Et$_2$-2,3,2-S$_4$ systems where ligand oxidation interfered at the highest applied potentials; vide infra). Thus, the electrochemical reversibility of each of these systems was firmly established.

The Cu^{II}L absorbance values were measured at the peak maximum in the vicinity of 400 nm where Cu^{I}L does not absorb and the absorbance of excess aquocopper(II) ion is insignificant. The absorbance values for each half-cycle (involving either the stepwise reduction or oxidation) were then plotted as a function of the applied potential according to the Nernst relationship:

$$E_{applied} = E^f - \frac{RT}{n\mathscr{F}} \ln\left(\frac{[Cu^I L']}{[Cu^{II} L']}\right) =$$

$$E^f + \frac{2.303\,RT}{n\mathscr{F}} \log\left[\frac{(A - A_R)}{(A_O - A)}\right] \quad (3)$$

In this expression, E^f represents the formal potential for the Cu$^{II/I}$L system at $\mu = 0.10$ M, [Cu^{I}L'] and [Cu^{II}L'] represent the sums of the molar concentrations of all forms of the complexes for each

(8) Ferris, N. S.; Woodruff, W. H.; Rorabacher, D. B.; Jones, T. E.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1978**, *100*, 5939–5942.

(9) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 4175–4180. Cf.: Lever, A. B. P. *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984; p 305.
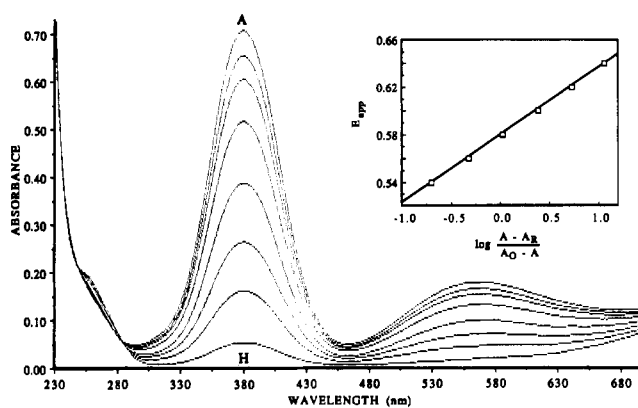

Figure 2. UV–visible absorption spectra for Cu^{II}([14]aneS$_4$) as a function of applied potential in aqueous solution at 25 °C, 0.10 M HClO$_4$ ($C_{Cu} = 9.94 \times 10^{-3}$ M; $C_L = 1.1 \times 10^{-4}$ M). Identification of curves (all potentials vs SHE): A, 0.80 V; B, 0.64 V; C, 0.62 V; D, 0.60 V; E, 0.58 V; F, 0.56 V; G, 0.54 V; H, 0.40 V. The inset shows a plot of applied potential as a function of Cu^{II}([14]aneS$_4$) absorbance at 390 nm. The slope of the regression line is 0.0564 ± 0.0005 V while the intercept, representing E^f, is 0.5757 ± 0.0003 V.

of the two oxidation states of copper (vide infra), A_O represents the absorbance of the fully oxidized solution (i.e., Cu^{II}L′), A_R represents the residual absorbance of the fully reduced solution, and A represents the absorbance measured at each applied potential. For Cu$^{II/I}$([16]aneS$_4$) and Cu$^{II/I}$(Et$_2$-2,3,2-S$_4$), the absorbance values for the totally reoxidized solution (A_O) were estimated since some oxidation of the ligand occurred at the highest applied potentials, +0.97 and +0.82 V (vs SHE), respectively. In all cases, linear plots of eq 3 were obtained with Nernstian slopes and essentially identical E^f values were obtained from the intercepts for both stepwise reduction and stepwise oxidation. The resultant E^f values are listed in Table I.

Potentiostatic determinations of the E^f values were also attempted for the complexes formed with [12]aneS$_4$ and [13]aneS$_4$. However, during the several hours that were required to perform an entire cycle, a precipitate was observed to form on the surface of the electrode (and sometimes on the bottom of the electrochemical cell), which resulted in erratic behavior. This precipitate formation was attributed to the exceptionally low aqueous solubility of these two ligands and their copper(I) complexes. In the case of the [13]aneS$_4$ system, this material was characterized by means of its FTIR and NMR spectra and by elemental analysis and was found to be Cu^I([13]aneS$_4$)(ClO$_4$). Anal. Calcd: C, 25.89; H, 4.35; S, 30.72. Found: C, 26.48; H, 4.57; S, 29.78. It was not ascertained whether this material was monomeric or polymeric. Attempts to obtain the Cu$^{II/I}$L potentials for the [12]- and [13]aneS$_4$ systems by the potentiostatic method in aqueous
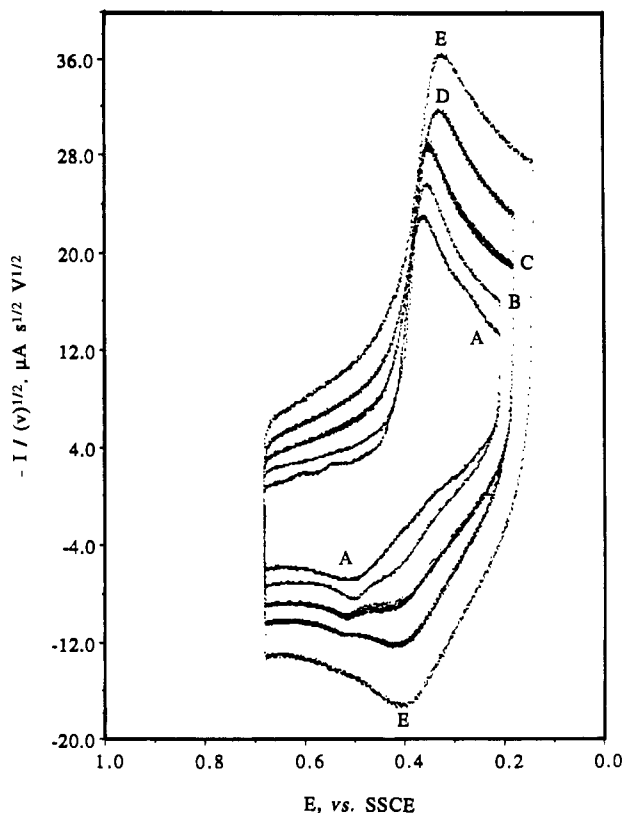
Figure 3. Cyclic voltammograms for an aqueous solution containing $Cu^{II}([12]aneS_4)$ in 0.10 M $HClO_4$ at a glassy-carbon electrode as a function of sweep rate at 25 °C ($C_{Cu} = 1.99 \times 10^{-3}$ M; $C_L = 3.1 \times 10^{-4}$ M; $[Cu^{II}L] = 2.3 \times 10^{-4}$ M). Scan rates in V s^{-1}: A, 0.010; B, 0.020; C, 0.050; D, 0.100; E, 0.200.

solution were subsequently abandoned.

Cyclic Voltammetric Studies. The cyclic voltammetric behavior of eight of the $Cu^{II/I}L$ systems was investigated both in aqueous solution and in 80% methanol (the ninth system, involving Me_2-2,3,2-S_4, being studied only in 80% methanol). For each system, an extended cyclic voltammogram was run initially at slow scan to establish the limits imposed by the potential at which the ligand begins to oxidize (an irreversible process) and the potential at which elemental copper begins to plate out on the electrode. These extended voltammograms were also used to identify the waves corresponding to the overall one-electron reduction and oxidation of the copper complex as represented in eq 2.

In subsequent cyclic voltammetric measurements on each system, the potential range was limited to include only that interval in which the complex itself was being oxidized and reduced. The sweep rate was generally varied from 10 mV s^{-1} up to 2–5 V s^{-1}, and the potentials and currents for both the cathodic and anodic peaks were determined. (These data are included in the supplementary material.)

The $Cu^{II/I}([15]aneS_4)$ system exhibited essentially reversible behavior at scan rates up to 500 mV s^{-1} in 80% methanol and up to 2 V s^{-1} in aqueous solution. The other systems studied tended to show an increase in the cathodic and anodic peak separation as a function of scan rate corresponding to quasi-reversible behavior.

Unique CV Behavior. Several examples of unique cyclic voltammetric behavior were noted. As previously reported,[2] both the $Cu^{II/I}([14]aneS_4)$ and $Cu^{II/I}([14]aneS_4$-diol) systems showed the development of a second anodic peak at more positive potentials as the scan rate was increased or as the temperature was decreased (to as low as −77 °C in 80% methanol). Under certain conditions, the development of a shoulder corresponding to a second cathodic peak at more positive potentials was also observed both in 80% methanol and, to a lesser extent, in aqueous solution. This behavior, which was extensively investigated, has been attributed to the presence of metastable intermediates of $Cu^{II}([14]aneS_4)$

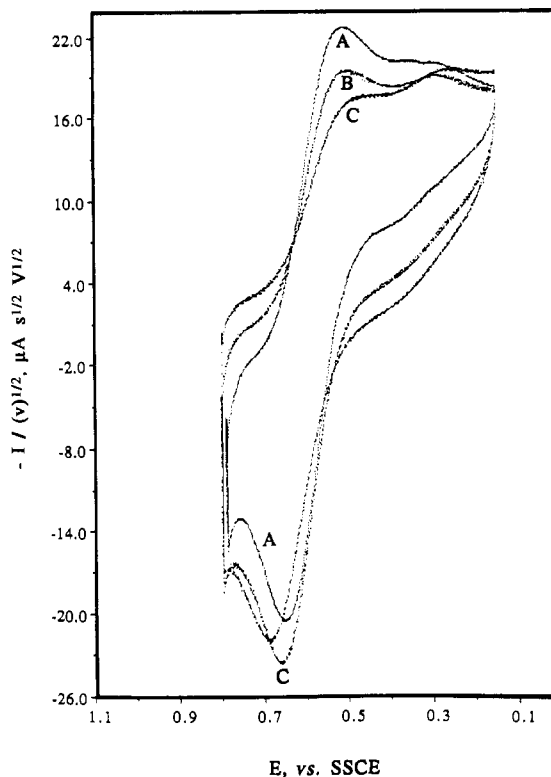**Figure 4.** Cyclic voltammograms for a solution containing $Cu^{II}(Et_2$-2,3,2-S_4) in 80% methanol, 0.10 M $HClO_4$, at a glassy-carbon electrode as a function of sweep rate at 25 °C ($C_{Cu} = 1.02 \times 10^3$ M; $C_L < 1 \times 10^{-3}$ M; $[Cu^{II}L] = 1.5 \times 10^{-4}$ M). Scan rates in V s^{-1}: A, 0.010; B, 0.050; C, 0.200.

and $Cu^I([14]aneS_4$-diol), which have been proposed to play a significant role in homogeneous electron-transfer reactions involving the copper polythia ether complexes.[2]

In contrast to the foregoing behavior, $Cu^{II}([12]aneS_4)$ solutions were observed to develop a second anodic peak at *more negative* potentials as the scan rate was increased in aqueous solution at 25 °C (Figure 3). In both 80% methanol and aqueous media, solutions of $Cu^{II}(Et_2$-2,3,2-S_4) exhibited two *cathodic* peaks. A more negative cathodic peak was observed to increase in height as the sweep rate was increased at room temperature (Figure 4). This peak then disappeared with the redevelopment of the more positive cathodic peak as the temperature was decreased to −22 °C.

The appearance of multiple anodic or cathodic peaks is suggestive of conformational control of the electron-transfer process as discussed in the following section. Unfortunately, both [12]-aneS$_4$ and Et$_2$-2,3,2-S$_4$ exhibit limited solubility, even in 80% methanol, so that the investigation of these phenomena was less extensive than the studies previously reported for the 14-membered macrocyclic ligand systems.[2]

Coupled Complexation Reactions. Due to the relatively small stability constants associated with the copper(II)–polythia ether complexes ($K_{Cu^{II}L} = 10^2$–10^5 M^{-1}), the cyclic voltammetric curves were generally measured on solutions containing a large excess of uncomplexed Cu^{2+} ion to force the complex formation reaction to the right:

$$Cu^{2+} + L \rightleftharpoons CuL^{2+} \qquad (4)$$
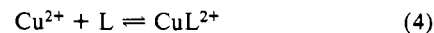
For solutions in which only stoichiometric quantities of Cu^{2+} and L were added, the ratio of the anodic to cathodic peak currents tended to be much larger than unity and the CV curves showed behavior indicative of a rapid preceding chemical reaction which was attributed to eq 4.

The half-wave potential ($E_{1/2}$) values obtained both in 80% methanol (by weight) and in aqueous solution from the slow-scan CV curves for all of the copper–polythia ether systems studied in this work are included in Table I. Corresponding values ob-

tained previously are also listed for comparison.

Anion Effects. In earlier work on the stability of the copper-(II)–polythia ether complexes, it has been noted that these complexes appear to become more stable upon the addition of increasing concentrations of anions that are normally considered to be "noncomplexing" (ClO_4^-, BF_4^-, $CF_3SO_3^-$). It has been shown that the observed behavior is not attributable to ion-pair formation nor is it observed with the NO_3^- ion. This phenomenon has been investigated extensively in the case of the perchlorate ion and has been found to result from the formation of an adduct between the $Cu^{II}L$ species and ClO_4^- (represented here simply as X^-)[10,11]

$$Cu^{II}L^{2+} + X^- \rightleftharpoons Cu^{II}LX^+ \qquad (5)$$
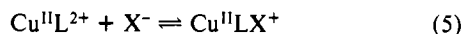
The $Cu^{II}LX^+$ adduct exhibits spectral properties identical with those of $Cu^{II}L^{2+}$. Within experimental error, both species also appear to exhibit the same kinetic properties in homogeneous electron-transfer reactions with counterreagents.[1] As noted above, the principal feature observed in solution is that the copper(II) complex appears to become more stable as perchlorate ion is added to the solution. Assuming that only the $Cu^{II}L$ species forms an adduct with perchlorate, the *observed formal potential values* should, therefore, decrease as the perchlorate concentration is increased.

To investigate the influence of $Cu^{II}LX^+$ formation upon the formal potential, the cyclic voltammetric behavior of the $Cu^{II/I}([14]aneS_4)$ system was investigated in 80% methanol as a function of the concentration of perchlorate ion over the range 0.05–1.0 M. The $E_{1/2}$ values did, in fact, decrease both for $Cu^{II}L$ solutions and $Cu^{I}L$ solutions in the following manner (listed in the order $[ClO_4^-]$; $E_{1/2}$, reduction; $E_{1/2}$, oxidation): 1.00 M, 0.62 V, 0.64 V; 0.50 M, 0.64 V, 0.66 V; 0.10 M, 0.69 V, 0.69 V; 0.05 M, 0.70 V, 0.71 V. Since the ionic strength also varied in these test solutions, a portion of this trend is attributable to changes in the relative activity coefficients for the two oxidation states. However, as shown in the next section, correcting for the activity coefficients reveals that a specific perchlorate interaction does exist with the $Cu^{II}L$ species.

Discussion

Formal Potential Values. The data in Table I show a reasonable level of consistency among the formal potential values generated in this work for each of the copper–polythia ether systems by means of the potentiostatic and cyclic voltammetric measurements on both $Cu^{II}L$ and $Cu^{I}L$ solutions. Values previously reported for the copper–polythia ether complexes in both water and 80% methanol are included in this table (as italicized values) for comparison. Whereas all of the previous values are qualitatively similar to the newly determined values, there are some significant differences. In all cases, other than for the $Cu^{II/I}([12]aneS_4)$ system (which does not appear to be fully equilibrated at the slowest scan rates, vide infra), the results from the current work are to be preferred due to the exceptional care taken in making these measurements.

With the exception of the Et_2-2,3,2-S_4 system, the maximum range among the aqueous potential values determined in the current work for any system is about 0.04 V. Whereas this level of discrepancy is tolerable, it is nonetheless disappointing, and the question inevitably arises as to which set of values is the most reliable. Intrinsically, the potentiostatic method should provide optimal values. Unfortunately, for both the $Cu^{II/I}(Et_2$-2,3,2-$S_4)$ and $Cu^{II/I}([16]aneS_4)$ systems, some ligand oxidation appeared to occur during the potentiostatic measurements before the complex itself was fully converted back to the $Cu^{II}L$ species (vide supra), thus making it necessary to estimate the final value of A_O in eq 3.

For the cyclic voltammetric studies, the $E_{1/2}$ values obtained from solutions containing $Cu^{II}L$ and those containing $Cu^{I}L$ are

Table II. Comparative Values for the Stability Constants of the Cu(II)– and Cu(I)–Polythia Ether Complexes in Aqueous Solution at 25 °C, 0.10 M ClO_4^-

complexed ligand	E^f, V vs SHE	$K_{CuIL'}/K_{CuIIL'}$ calcd	$K_{CuIIL'}$ exptl[a]	$K_{CuIL'}$ calcd[b]
$[12]aneS_4$	<0.69	$<3 \times 10^9$	$2.4_7 \times 10^3$	$<7 \times 10^{12}$
$[13]aneS_4$	≈0.52	$≈3.9 \times 10^6$	$2.7_7 \times 10^3$	$≈1._1 \times 10^{10}$
$[14]aneS_4$	0.59	6.0×10^7	$2.1_8 \times 10^4$	1.3×10^{12}
$[14]aneS_4$-diol	0.52	3.9×10^6	1.3×10^{3c}	$5._1 \times 10^9$
$[15]aneS_4$	0.64	4.2×10^8	$1.4_9 \times 10^3$	6.2×10^{11}
$[16]aneS_4$	0.71	4.3×10^9	$1.6_0 \times 10^2$	1.0×10^{12}
$[15]aneS_5$	0.69	4.3×10^9	$1.5_3 \times 10^4$	4.5×10^{13}
Me_2-2,3,2-S_4	≈0.79	$≈1.4 \times 10^{11}$	9.4×10	$≈1._3 \times 10^{13}$
Et_2-2,3,2-S_4	0.79	1.4×10^{11}	$1.5_1 \times 10^2$	$2._2 \times 10^{13}$

[a] All values from ref 10 except as noted. [b] All values calculated by using eq 8. [c] Reference 7.

generally within experimental error for each system. Since the influences of the kinetic parameters for the conformational changes in the square scheme are generally manifested differently in $Cu^{II}L$ and $Cu^{I}L$ solutions,[2] this similarity in itself serves as partial reassurance that the $E_{1/2}$ values obtained by CV at slow scan rates are valid measures of the overall formal potential values. However, our analysis of the phenomenon leading to the appearance of the additional anodic peak observed to develop in the $Cu^{II/I}([12]aneS_4)$ system at reasonably slow scan rates, as discussed below, suggests that the observed $E_{1/2}$ value for this system does not represent an equilibrated condition even at the slowest scan rate used. For the $Cu^{II/I}(Et_2$-2,3,2-$S_4)$ system, the appearance of the CV curves in aqueous solution was indicative of $Cu^{II}L$ adsorption at the electrode surface. Thus, the apparent $E_{1/2}$ value for this system, as obtained from the CV studies, is considered to be unreliable.

On the basis of our analysis of the reliability of the experimental values obtained in this and our previous studies, a set of recommended formal potential values for aqueous solution at 25 °C, 0.1 M ClO_4^-, is included in the last column of Table I. These values are believed to be accurate to within ±0.01–0.02 V except as noted.

Stability Constants for Cu(I) Complexes. The stability constant for each of the $Cu^{II}L$ complexes, defined as

$$K_{Cu^{II}L'} = \frac{[Cu^{II}L']}{[Cu^{2+}][L]} \qquad (6)$$

where

$$[Cu^{II}L'] = [CuL^{2+}] + [CuLX^+] \qquad (7)$$

(vide infra) has been determined previously by means of careful spectrophotometric measurements.[10,11] From these values and the recommended E^f values listed in Table I, the stability constants for the corresponding $Cu^{I}L$ complex species can be calculated from the Nernst equation[12]

$$E^f = E_{aq}^{\circ\prime} - \frac{2.303RT}{n\mathcal{F}} \log \left(\frac{K_{Cu^{II}L'}}{K_{Cu^{I}L'}} \right) \qquad (8)$$

where $E_{aq}^{\circ\prime}$ represents the standard electrode potential for the Cu_{aq}^{2+}/Cu_{aq}^+ redox couple expressed in terms of concentrations and $[Cu^{I}L'] \approx [CuL^+]$. On the basis of a value of $E_{aq}^{\circ\prime} = 0.13$ V at 25 °C,[13] the $K_{Cu^{I}L}$ values have been calculated by using eq

(10) Sokol, L. S. W. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1981**, *20*, 3189–3195.

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

(12) Rorabacher, D. B.; Martin, M. J.; Koenigbauer, M. J.; Malik, M.; Schroeder, R. R.; Endicott, J. F.; Ochrymowycz, L. A. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 167–202.

(13) The "concentration potential" value was calculated by correcting the standard potential for the aquocopper(II/I) redox couple ($E^\circ = 0.153$ V: Milazzo, G.; Caroli, S. *Tables of Standard Electrode Potentials*; Wiley: New York, 1978) by the activity coefficients for the aquated ions at an ionic strength of 0.10 M, using the extended Debye–Hückel equation (assuming ionic diameters of 4 Å for each species). Use of the standard (activity) potential rather than the concentration potential value yields $K_{Cu^{I}L}$ values that are smaller by about a factor of 2.

8 and are listed in Table II.

The calculated K_{Cu^IL} values for the complexes formed with [14]-, [15]-, and [16]aneS$_4$ are seen to be essentially constant, being an order of magnitude smaller than the values for the acyclic ligands. This supports the contention that *there is no macrocyclic effect for Cu(I)* and demonstrates the insensitivity of Cu(I) to cavity size. The smaller K_{Cu^IL} values that are calculated for the [13]aneS$_4$ and [14]aneS$_4$-diol systems appear to be attributable to a reduction in the number of Cu–S bonds formed in the Cu^{I}L species. Unlike the larger macrocyclic systems, these ligands are judged to be incapable of coordinating all four sulfur donor atoms to the Cu(I) atom simultaneously. This conclusion was reached earlier in the case of the former system[1] and, for the latter system, is consistent with a recent crystal structure of Cu^{II}(*syn*-[14]-aneS$_4$-diol)(NO$_3$)$_2$[15] in which it has been found that the steric hindrance caused by the two *syn*-OH moieties results in a complex in which the Cu(II) ion is five-coordinate with the copper sitting above the plane of the four sulfur donor atoms in a manner analogous to that found for the [12]- and [13]aneS$_4$ complexes.[16] This analogy suggests that the *syn*-[14]aneS$_4$-diol would also be incapable of coordinating all four sulfur donor atoms in a tetrahedral array around the Cu(I). This analysis further suggests that a similarly small K_{Cu^IL} value should apply for the Cu^I-([12]aneS$_4$) complex and would dictate that the correct E^f value for this latter system should be approximately 0.52 V.

For the Cu^I([15]aneS$_5$) complex, which exhibits a significantly larger K_{Cu^IL} value, the crystal structure has shown that four of the sulfur donor atoms are bonded to the Cu(I) ion in a slightly distorted tetrahedral array.[17] Moreover, the ^{1}H NMR spectrum for this Cu(I) complex reveals that all five sulfurs are equivalent on the NMR time scale,[18] indicating that all five sulfur atoms spend equal time being bonded to the Cu(I). This *resonance* phenomenon may stabilize this species and account for the larger K_{Cu^IL} value observed.

Conformational Effects. As noted in the preceding section, Cu^{II}([12]aneS$_4$) solutions were observed to develop a second anodic peak at *more negative* potentials as the scan rate was increased in aqueous solution at 25 °C (Figure 3). This behavior is similar to that reported previously for Cu^{II}([14]aneS$_4$) solutions at fast scan rates and low temperature (−77 °C).[2] For the latter system, this phenomenon was attributed to the slow equilibration of the two Cu^{I}L species designated as P and R in eq 1. The P conformer is believed to be in a distorted geometry more closely approximating that of the stable Cu^{II}L species (O) and is oxidized at a more negative potential. Therefore, under very slow scan conditions, the P conformer is oxidized first on the anodic sweep and the R conformer is continuously converted to P so that the single anodic peak observed is presumably representative of the equilibrated PR pair. As the scan rate is increased to a level where it becomes comparable to the rate constant k_{RP}, however, the amount of P existing in solution is immediately reduced on the anodic sweep but the R conformer does not have time to convert to P before the potential reaches a value at which R itself is oxidized directly to Q. Since R is the more stable Cu^{I}L species, there is more R to oxidize than P and the R → Q peak (i.e., the more positive peak) is dominant on the anodic half-cycle.[2]

This latter situation would appear to have been reached in the Cu$^{II/I}$([12]aneS$_4$) system at the slowest scan rates measured since only the more positive anodic peak is observed even at a sweep rate of 10 mV s^{-1}. (The fact that this is not an *equilibrated* anodic peak is indicated by the large separation of the cathodic and anodic peaks, amounting to 156 mV, at the slowest scan rate observed: see supplementary material.) As the scan rate is increased on a solution initially containing only Cu^{II}L, the P conformer produced by the reduction of O during the cathodic half-cycle presumably does not have time to convert to the more stable R conformer before it is reoxidized on the return sweep. This would account for the redevelopment of the more negative anodic peak as the scan rate is increased (Figure 3). Since this same behavior did not appear in the Cu$^{II/I}$([14]aneS$_4$) system until the temperature was lowered to −77 °C (in 80% methanol), we conclude that the P $\rightleftharpoons$ R interconversion must be *much* slower in the Cu$^{II/I}$([12]aneS$_4$) system to permit its observation at 25 °C. Thus, the $E_{1/2}$ value observed for this system, even at the slowest scan rates utilized, is presumably *not* the equilibrated E^f value.

In the case of the Cu$^{II/I}$(Et$_2$-2,3,2-S$_4$) system in 80% methanol, two cathodic peaks are observed, the more negative peak emerging as the scan rate is increased at room temperature (Figure 4). When the temperature is decreased (equivalent to a further increase in the scan rate), the more negative cathodic peak disappears while the more positive peak redevelops and ultimately becomes dominant at −22 °C. The behavior of these peaks does not appear to be characteristic of a situation involving adsorption at the electrode surface (as was observed for this same system in aqueous solution). Moreover, the observed temperature behavior is *not* analogous to the corresponding anodic peak behavior observed earlier for the Cu$^{II/I}$([14]aneS$_4$) system. In that system, the redevelopment of a peak apparently associated with the metastable intermediate (P) at low temperature was only observed in the case where the bulk solution contained predominantly the stable Cu^{II}L species (O) and the metastable Cu^{I}L species (P) formed was too sluggish, at low temperature, to convert to the more stable Cu^{I}L species (R) before being reoxidized on the anodic sweep. The corresponding behavior on the cathodic sweep for the Et$_2$-2,3,2-S$_4$ system should only be observed for solutions containing primarily Cu^{I}L. For a Cu^{II}L solution, as shown in Figure 4, rapid scan rates or low temperature should exhibit *only* the development of the cathodic peak representing the reduction of the stable Cu^{II}L species (O) if it were analogous to the [14]aneS$_4$ system.

The cathodic peak behavior observed for the Et$_2$-2,3,2-S$_4$ system at low temperature may be attributable to the very small Cu^{II}L stability constant associated with this acyclic ligand. Due to the instability of the Cu^{II}(Et$_2$-2,3,2-S$_4$) complex, much of the Cu^{II}L species is dissociated in solution at 25 °C. At slow scan rates, the system is fully equilibrated at all times and a single cathodic peak is observed. As the scan rate is increased, however, the Cu^{II}L complex is depleted in the vicinity of the electrode faster than additional complex can form, and it is possible that the second peak, which is observed to develop at more negative potentials, corresponds to the reduction of free Cu$_{aq}^{2+}$, this latter reduction being driven by reaction of Cu$_{aq}^+$ with free ligand to form Cu^{I}L. Analysis of this more negative peak in terms of the treatment of Nicholson and Shain[19] confirms the fact that its behavior corresponds to a system involving a succeeding chemical reaction in approximate accordance with the calculated stability constant for Cu^{I}L and the presumed rate constant for its formation. In fact, with a very large excess of Cu^{2+}(aq) present, the behavior of this system becomes more *normal* (see supplementary material).

On the basis of foregoing hypothesis, the disappearance of the second cathodic peak in the Et$_2$-2,3,2-S$_4$ system as the temperature is lowered may be attributed to a reduction in the formation rate constant for the Cu^{I}L complex. When the formation rate of this species becomes slower than the time duration of the sweep, this following chemical reaction is no longer significant on the cyclic voltammetric time scale so that no direct reduction of Cu^{2+}(aq) to Cu^{I}L is observed. Confirmation of this hypothesis must await more extensive experimental evidence.

(14) A crystal structure of the Cu^I([14]aneS$_4$) complex showed only three sulfur donor atoms from a single ligand coordinated to the Cu(I) with the fourth coordination site occupied by a sulfur donor atom from an adjacent ligand to form a 3:1 coordination polymer (Diaddario, L. L., Jr.; Dockal, E. R.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1985**, *24*, 356–363.)

(15) Meagher, N. E.; Heeg, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. Unpublished results.

(16) 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.

(17) 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.

(18) Vande Linde, A. M. Q. Ph.D. Dissertation; Wayne State University: Detroit, MI, 1988.

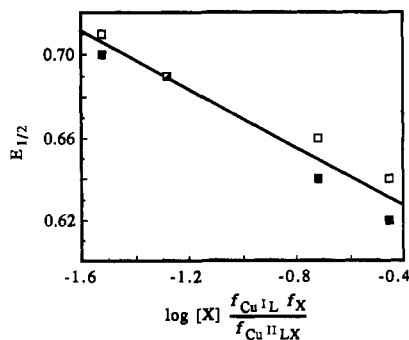(19) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706–723.

Figure 5. Plot of eq 13' showing the trend of the formal potential value for the $Cu^{II/I}([14]aneS_4)$ system as a function of perchlorate ion concentration in 80% methanol. The solid figures were obtained from the reduction of $Cu^{II}L$ while the open figures were obtained from the oxidation of $Cu^{I}L$. The regression line shown has a slope of 0.070 and an intercept of 0.60 V, the latter value presumably representing the corrected standard potential for this system.

Perchlorate Effect. The measurements made on the $Cu^{II/I}$-$([14]aneS_4)$ system in 80% methanol, as given in the Results section, show a decrease in the formal potential value for this system as the perchlorate ion concentration is increased. This is consistent with a stabilization of the $Cu^{II}L$ species or a destabilization of the $Cu^{I}L$ species.

From carefully conducted equilibrium studies, we have previously shown that the equilibrium constant for reaction 5, expressed as

$$K_{1X}^0 = \frac{[Cu^{II}LX^+]}{[Cu^{II}L^{2+}][X^-]}\left(\frac{f_{Cu^{II}LX}}{f_{Cu^{II}L}f_X}\right) \qquad (9)$$

has a relatively consistent value of $K_{1X}^0 \approx 20$ in aqueous solution at 25 °C for all of the copper(II)-tetrathia ether complexes[11] (by contrast, $K_{1X}^0 \approx 0$ for the $Cu^{II}([15]aneS_5)$ complex where the Cu(II) ion is fully coordinated by the ligand). This implies that, in the presence of 0.10 M ClO_4^- ion (the general conditions used in this study), two-thirds of the $Cu^{II}L$ species should be present in the form of the $Cu^{II}LX^+$ adduct. Since it has been presumed that the $Cu^{I}L$ species does not form a similar adduct with perchlorate, the trend in the formal potential values for the $Cu^{II/I}$-$([14]aneS_4)$ system is qualitatively consistent with our predictions.

To obtain a quantitative evaluation of the perchlorate adduct formation, the Nernst expression for eq 2 may be written in terms of the (thermodynamic) standard potential, $E°$, as

$$E = E° - \frac{RT}{n\mathscr{F}}\ln\left(\frac{a_{Cu^{I}L}}{a_{Cu^{II}L}}\right) =$$

$$E° - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[Cu^{I}L]}{[Cu^{II}L]}\left(\frac{f_{Cu^{I}L}}{f_{Cu^{II}L}}\right)\right) \qquad (10)$$

where $a_{Cu^{I}L}$ and $a_{Cu^{II}L}$ represent the activities of $Cu^{I}L$ and $Cu^{II}L$, respectively, and $f_{Cu^{I}L}$ and $f_{Cu^{II}L}$ represent the activity coefficients for the corresponding copper complexes. Substitution of eqs 7–9 into eq 10 yields

$$E = E° - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[Cu^{I}L]}{[Cu^{II}L']}\alpha_{Cu^{II}L}\left(\frac{f_{Cu^{I}L}}{f_{Cu^{II}L}}\right)\right) \qquad (11)$$

where[20]

$$\alpha_{Cu^{II}L} = [Cu^{II}L']/[CuL^{2+}] = 1 + K_{1X}^0[X^-](f_{Cu^{II}L}f_X/f_{Cu^{II}LX}) \qquad (12)$$

(20) The quantity $\alpha_{Cu^{II}L}$ is defined here as the reciprocal of the fractional concentration of CuL^{2+} in solution in accordance with Ringbom's convention: Ringbom, A. *Complexation in Analytical Chemistry*; Interscience: New York, 1963.

From a comparison of eqs 3 and 11, it is apparent that

$$E^f = E° - \frac{2.303RT}{n\mathscr{F}}\log\left[\alpha_{Cu^{II}L}\left(\frac{f_{Cu^{I}L}}{f_{Cu^{II}L}}\right)\right] \qquad (13)$$

A plot of $E_{1/2}$ $(\approx E^f)$ vs the quantity $\log[\alpha_{Cu^{II}L}(f_{Cu^{I}L}/f_{Cu^{II}L})]$ should yield a slope of $-2.303RT/n\mathscr{F}$ (i.e., -0.059 at 25 °C) and an intercept of $E°$. Although the value of K_{1X}^0 has not been evaluated in 80% methanol, it can be initially approximated by the aqueous value (i.e., $K_{1X}^0 \approx 20$) since the ion-pairing contribution is small. When this approximation is used, the plot obtained is reasonably linear with a negative slope (-0.15), which is much larger than the theoretical value. The latter feature suggests that the K_{1X}^0 value in 80% methanol is, in fact, significantly larger than the aqueous value.

If K_{1X}^0 increases in 80% methanol to the point where the $Cu^{II}LX$ species becomes dominant, the Cu(II)/(I) redox half-reaction can be represented by the alternate form
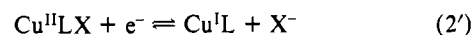
$$Cu^{II}LX + e^- \rightleftharpoons Cu^{I}L + X^- \qquad (2')$$

for which the Nernst equation may be written as

$$E = E° - \frac{RT}{n\mathscr{F}}\ln\left(\frac{[Cu^{I}L][X^-]}{[Cu^{II}LX]}\left(\frac{f_{Cu^{I}L}f_X}{f_{Cu^{II}LX}}\right)\right) \qquad (10')$$

Assuming that $E_{1/2}$ represents the solution condition where $[Cu^{I}L]$ $= [Cu^{II}LX]$

$$E_{1/2} = E° - \frac{2.303RT}{n\mathscr{F}}\log\left([X^-]\left(\frac{f_{Cu^{I}L}f_X}{f_{Cu^{II}LX}}\right)\right) \qquad (13')$$

a plot of $E_{1/2}$ vs $\log[X^-]$ $(f_{Cu^{I}L}f_X/f_{Cu^{II}LX}))$ should then yield a linear relationship with the anticipated Nernstian slope (-0.059). Figure 5 shows such a plot, for which the slope is -0.070 and the intercept is 0.60. In view of the variation in the measured potential values, this slope must be considered to be within experimental error of the Nernstian value. Therefore, in view of the treatment used in generating this plot, we conclude that the perchlorate adduct is considerably more stable in 80% methanol than in aqueous solution. In fact, it is noteworthy that the corrected $E°$ value in 80% methanol is within experimental error of the aqueous E^f value for this system.

Since corrections for the perchlorate adduct have not been made in the other studies reported in this work, the formal potential values, as defined in eq 3, have been based on the total concentration of Cu^{II} complexed to the ligand, designated as $Cu^{II}L'$. Thus, the recommended potential values listed in the last column of Table I are strictly valid only for 0.10 M ClO_4^-, although past evidence would suggest that similar values would apply in 0.10 M BF_4^- or $CF_3SO_3^-$. However, in aqueous solution, where the extent of perchlorate adduct formation is much smaller than in 80% methanol, the recommended formal potential values should be approximately correct for other conditions as well.