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Effect of "Noncomplexing" Anions on Copper(II)-Macrocyclic Tetrathiaether Complexes. Evaluation of Dissociation Kinetics in Aqueous Solution Using Mercury(II) Ion as Scavenger

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As a follow-up to earlier work which indicated that copper(II)-macrocyclic tetrathiaether complexes are stabilized by the presence of anions normally considered to be noncomplexing, the dissociation kinetics of Cu(II) complexes with [12]aneS_4, [13]aneS_4, and [14]aneS_4 have been investigated in aqueous solution at 25 °C as a function of perchlorate ion concentration using aquamercury(II) ion as the scavenging species. For the Cu^{II}([14]aneS_4) complex, additional kinetic studies have been conducted in the presence of tetrafluoroborate, trifluoromethanesulfonate, and nitrate ions. For all systems, the kinetic data are interpreted to represent a combination of the direct $Cu^{II}L$ complex dissociation pathway plus a parallel pathway in which the Hg(II) actively displaces the Cu(II) from the ligand, presumably by forming coordinate bonds to the ligand before $Cu^{II}L$ is fully dissociated. Both the direct $Cu^{II}L$ dissociation rate and the Hg(II) displacement rate decrease markedly upon increasing the concentration of the perchlorate, tetrafluoroborate, and trifluoromethanesulfonate ions but show no dependence upon nitrate ion. For the studies involving variable perchlorate ion concentration, two specific dissociation rate constants (k^{CuL} and k^{CuLX}) are resolved representing the dissociation of CuL^{2+} and the anion adduct $CuLX^+$ (where X^- represents ClO_4^-); in addition, two specific mercury(II) displacement rate constants (${k_{Hg}}^{CuL'}$ and ${k_{Hg}}^{CuLX'}$, both expressed as first-order rate constants after correction for outer-sphere complex formation) are resolved for these same two Cu(II) complex species. The resultant values at 25 °C for all four specific rate constants (s^{-1}), listed in the order k^{CuL}, k^{CuLX}, ${k_{Hg}}^{CuL'}$, and ${k_{Hg}}^{CuLX'}$ are as follows: Cu^{II}([12]aneS_4), 8 ± 2, 1.3 ± 0.4, (2.6 ± 0.3) × 10^3, (9 ± 6) × 10^1; Cu^{II}([13]aneS_4), 95 ± 11, 9 ± 2, (1.0 ± 0.1) × 10^4, (4 ± 1) × 10^3; Cu^{II}([14]aneS_4), 18 ± 2, 1.2 ± 0.3, (1.4 ± 0.3) × 10^3, (5.3 ± 0.6) × 10^2. The mechanistic implications of the observed kinetic effects for these "noncomplexing" anions are discussed.

Introduction

In previous work in our laboratory,[2,3] the stability constants for the entire homologous series of Cu(II) complexes formed with tetrathiacycloalkanes ranging from 12- to 16-membered macrocycles (e.g., see Figure 1) as well as the corresponding open-chain species have been determined as a function of temperature in aqueous solution:

$$Cu^{2+} + L \rightleftharpoons CuL^{2+} \qquad K_{CuL} \tag{1}$$

Since the polythiaether ligands do not protonate, the stability constants of the Cu(II) complexes are independent of acidity over the range of pH from 0 to >8.[4] In the process of making these measurements, however, we noted an unusual enhancement in the complex stability constants caused by the presence of anions normally considered to be noncomplexing, including perchlorate, trifluoromethanesulfonate, and tetrafluoroborate.[2,3] This phenomenon has been attributed to the formation of a ternary complex between the $Cu^{II}L$ complexes and the anion X^-:

$$CuL^{2+} + X^- \rightleftharpoons CuLX^+ \qquad K_{1X} \tag{2}$$

Since the visible absorption spectra of CuL^{2+} and $CuLX^+$ appear to be indistinguishable,[2] the net result of reactions 1 and 2 is that an increase in [X^-] results in an apparent increase in the spectrophotometrically observed overall stability constant of the copper(II) complex, designated as $K_{CuL'}$:

$$Cu^{2+} + L \rightleftharpoons CuL' \qquad K_{CuL'} \tag{3}$$

where

$$[CuL'] = [CuL^{2+}] + [CuLX^+] \tag{4}$$

Corresponding stability constant measurements on the Cu(II) complex formed with a closely related macrocyclic pentathiaether ligand, [15]aneS_5, revealed that no such anion effects were present.[3] In the latter complex, Cu(II) is 5-coordinate with all inner-sphere sites occupied by ligand donor atoms,[5] whereas the Cu(II)-tetrathiaether complexes contain one or two coordinated water molecules depending upon the ring size.[6] These considerations led to the conclusion that the $CuLX^+$ adduct formed with tetrathiaether ligand complexes involves an inner-sphere interaction between Cu(II) and X^-.[3] That interactions of this type have rarely been reported is presumably due to the fact that such interactions are not generally investigated.[7] Moreover, most ligands are protonatable and/or charged, and any alterations in the observed $Cu^{II}L$ properties with changing concentrations of "inert" salt would generally be attributed simply to ionic strength effects. Although the formation of anion adducts may be unique to polythiaether complexes, the possibility that many Cu(II)-ligand systems may contain a mixture of $Cu^{II}L$ and $Cu^{II}LX$ species in solution, combined with the possibility that these two species may exhibit different chemical and physical properties, suggests that the characterization of these ternary interactions may be of general significance. Therefore, it was deemed highly desirable to obtain additional insight into the nature of these anion interactions with the copper-tetrathiaether complexes. Accordingly, we have now undertaken an investigation of the effect of such anions upon the complexation kinetics of these Cu(II) systems.

The limited solubility of the polythiaether ligands hampers direct measurement of the Cu(II) complex formation kinetics in aqueous solution. To circumvent this problem, extensive kinetic investigations of the formation and dissociation of the copper(II)-polythiaether complexes were conducted in our laboratory several years ago, in the presence of 0.10 M perchlorate ion, using a wide range of methanol-water solvent mixtures:[8]

$$Cu^{2+} + L \underset{k_d}{\overset{k_f}{\rightleftharpoons}} CuL' \tag{5}$$

From the trends observed as a function of solvent composition, it proved possible to extrapolate the apparent k_f and k_d values for all ligand systems to aqueous conditions.

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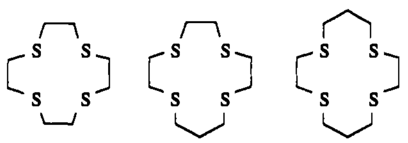

[12]aneS$_4$ [13]aneS$_4$ [14]aneS$_4$

Figure 1. Ligands studied in this work.

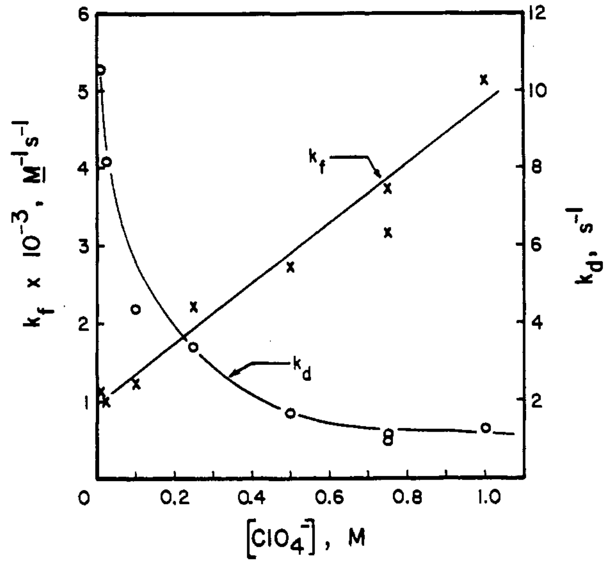

Figure 2. Dependence of the formation and dissociation rate constants for the Cu^{II}([12]aneS$_4$) complex on perchlorate ion in 80% methanol at 25 °C.

Prior to undertaking the current studies, we conducted a series of similar kinetic measurements in which the perchlorate ion concentration was varied in a single solvent composition, 80% methanol–20% water (by weight).[9] The results revealed that k_f increases linearly with increasing ClO_4^- concentration while the dissociation rate constant decreases rapidly as the concentration level of ClO_4^- increases, after which these rate constants appear to level off. The trends for both rate constants are illustrated in Figure 2 for the reaction of solvated Cu(II) ion with [12]aneS$_4$. Unfortunately, the large number of solvated species of the metal ion {e.g., $Cu(H_2O)_6^{2+}$, $Cu(H_2O)_5(CH_3OH)^{2+}$, $Cu(H_2O)_4(CH_3OH)_2^{2+}$, etc.}, the copper complex {$CuL(H_2O)_2^{2+}$, $CuL(H_2O)(CH_3OH)^{2+}$, $CuL(CH_3OH)_2^{2+}$}, and the ternary complex {$CuLX(H_2O)^+$, $CuLX(CH_3OH)^+$} existing in mixed methanol-water solvents makes it impossible to assign specific trends in kinetic behavior to individual solvated Cu(II), Cu^{II}L, or Cu^{II}LX species. Moreover, in order to extrapolate to aqueous conditions, it would be necessary to conduct an inordinately large number of kinetic measurements in which $[ClO_4^-]$ is varied in a wide range of solvent mixtures.

Attempts to obtain complex formation rate data directly in aqueous solution continue to be thwarted by the limited solubility of the free ligands in water (except in the case of recently studied alcoholic derivatives).[10] However, since the Cu(II) complexes formed with the polythiaether ligands are much more soluble in water than are the free ligands, it was concluded that it should be possible to determine the dissociation rate constants directly in aqueous solution provided that some means were available to promote complex dissociation. In the current study we have used the aquated Hg(II) ion as a scavenger for the ligand according to the overall reaction

$$CuL' + Hg_{aq}^{2+} \rightleftharpoons Cu_{aq}^{2+} + HgL^{2+} \qquad (6)$$

As a scavenging ion, Hg(II) has the double advantage of reacting very quickly in forming metal–ligand complexes[11] as well as forming very stable complexes with the cyclic polythiaether ligands,[12] thereby driving reaction 6 to the right. Not surprisingly, however, two competitive mechanistic pathways exist. The first pathway involves the direct dissociation of the Cu^{II}L complex followed by rapid scavenging of the dissociated ligand by Hg(II), while the second involves a direct attack by Hg(II) on the Cu^{II}L complex to form a mixed CuLHg species which then promotes the displacement of Cu(II) from the ligand:

direct dissociation pathway

$$CuL' \underset{k_f}{\overset{k_d}{\rightleftharpoons}} Cu^{2+} + L \qquad (5')$$

$$Hg^{2+} + L \overset{k_{Hg}^{L}}{\rightleftharpoons} HgL^{2+} \quad \text{(rapid)} \qquad (7)$$

mercury(II) displacement pathway

$$CuL' + Hg^{2+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} CuLHg' \qquad (8)$$

$$CuLHg' \xrightarrow{k_2} Cu^{2+} + HgL^{2+} \quad \text{(rapid)} \qquad (9)$$

Since the latter pathway is dependent upon the concentration of Hg^{2+} whereas the former pathway is not, the relative contributions of the two pathways to the overall kinetics can be determined by varying $[Hg^{2+}]$.

For the current study, we have examined the overall Hg(II)–Cu^{II}L exchange kinetics in aqueous solution for the copper(II) complexes formed with the three macrocyclic tetrathiaether ligands depicted in Figure 1: 1,4,7,10-tetrathiacyclododecane ([12]aneS$_4$), 1,4,7,10-tetrathiacyclotridecane ([13]aneS$_4$), and 1,4,8,11-tetrathiacyclotetradecane ([14]aneS$_4$). Rate constants representing both the direct dissociation and mercury(II) ion displacement pathways have been resolved for all systems as a function of anion concentration.

Experimental Section

Copper(II) perchlorate was prepared by the dropwise addition of 70% $HClO_4$ (G. F. Smith Chemical Co.) to a stirred slurry of reagent grade $CuCO_3$ (Mallinckrodt Inc.), followed by evaporation, crystallization, and filtration. [*WARNING! Copper(II) perchlorate may be explosive if heated to remove waters of crystallization!*] This material was then recrystallized twice from water. Copper(II) tetrafluoroborate and trifluoromethanesulfonate solutions were prepared directly by the reaction of reagent grade $CuCO_3$ with stoichiometric amounts of HBF_4 (Aldrich Chemical Co.) and CF_3SO_3H (3M Corp.), respectively, the latter acid being purified by vacuum distillation immediately before use. Reagent grade copper(II) nitrate (Fisher Scientific) was used without further purification in the preparation of all copper nitrate solutions. Copper(II) solutions were standardized by EDTA titration using murexide indicator. Mercury(II) solutions were prepared by dissolving weighed amounts of reagent grade HgO (Fisher Scientific) in the appropriate acid solutions and diluting to volume. The resulting mercury(II) concentrations were determined by potentiometric titration with EDTA using a Reilley mercury pool sensing electrode. Copper(II)–tetrathiaether solutions were prepared by adding a weighed portion of the tetrathiaether ligand to a solution containing excess Cu(II) salt and stirring overnight. Undissolved ligand was then filtered off. Since all kinetic measurements were made under conditions where the Hg(II) ion was in large excess, determination of the exact Cu(II) complex concentration was unnecessary. Conductivity grade deionized–distilled water was used in the preparation of all solutions.

Kinetic studies were carried out using a Durrum Model D-110 stopped-flow spectrophotometer equipped with glass and Kel-F tubing and fittings, the temperature being controlled at 25.0 ± 0.2 °C with a Forma-Scientific circulating water bath. The instrumental response was recorded on a Biomation Model 802 transient recorder from which the

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Table I. Resolved Dissociation and Mercury(II) Displacement Rate Constants for Copper(II) Macrocyclic Tetrathiaether Complexes as a Function of Perchlorate Ion Concentration in Aqueous Solution at 25 °C[a]

	[12]aneS_4[b]		[13]aneS_4[b]		[14]aneS_4[b]	
[ClO_4^-], M	k_d, s^{-1}	$k_1 \times 10^{-3}$, $M^{-1}\ s^{-1}$	k_d, s^{-1}	$k_1 \times 10^{-3}$, $M^{-1}\ s^{-1}$	k_d, s^{-1}	$k_1 \times 10^{-3}$, $M^{-1}\ s^{-1}$
0.05	4.2 (4)	2.1 (2)	43 (1)	12.8 (5)	11.1 (4)	1.0 (1)
			62 (3)	14.6 (9)	11.7 (2)	1.17 (5)
0.10	3.7 (5)	3.04 (7)	56 (1)	10.5 (2)	7 (1)	2.5 (1)
	5.3 (3)	1.72 (6)	56 (2)	11.9 (4)	11.4 (5)	1.61 (6)
	4.8 (4)	1.59 (7)				
0.25	3.7 (4)	1.75 (6)	36 (2)	15.4 (3)	4.8 (4)	2.25 (3)
0.50	3.2 (3)	1.48 (5)	22 (3)	18.7 (5)	4.1 (7)	2.37 (4)
0.75	1.9 (4)	1.30 (6)	23 (1)	18.8 (3)		
1.00	0.6 (3)	1.21 (5)	14.1 (4)	19.99 (9)	2.4 (6)	2.44 (4)

[a] For this and all subsequent tables, values in parentheses represent the standard deviations in terms of the last significant figure listed; e.g., 4.2 (4) represents 4.2 ± 0.4. [b] Analytical concentrations used: [12]aneS_4, $C_{Hg} \approx 0.5$–10 mM, $C_{Cu} \approx 0.55$ or 1.1 mM, $C_L \approx 0.042$ or 0.084 mM; [13]aneS_4, $C_{Hg} \approx 0.5$–10 mM, $C_{Cu} \approx 0.92$ mM, $C_L \approx 0.044$ mM; [14]aneS_4, $C_{Hg} \approx 1.5$–15 mM, $C_{Cu} \approx 0.55$ mM, $C_L \approx 0.021$ or 0.041 mM.

Table II. Resolved Dissociation and Mercury(II) Displacement Rate Constants for the Cu^{II}([14]aneS_4) Complex as a Function of the Concentration of Tetrafluoroborate, Trifluoromethanesulfonate, and Nitrate Ion in Aqueous Solution at 25 °C

	BF_4^-[a]		$CF_3SO_4^-$[a]		NO_3^-[a]	
[X^-], M	k_d, s^{-1}	$k_1 \times 10^{-3}$, $M^{-1}\ s^{-1}$	k_d, s^{-1}	$k_1 \times 10^{-3}$, $M^{-1}\ s^{-1}$	k_d, s^{-1}	$k_1 \times 10^{-3}$, $M^{-1}\ s^{-1}$
0.05					8.4 (4)	4.0 (1)
0.10	11.7 (3)	1.46 (4)	19.1 (8)[b]	1.1 (2)[b]	13.7 (6)	4.0 (1)
0.25			7.5 (4)	1.96 (9)		
0.50	4.3 (5)	2.36 (9)			14 (2)	9.0 (3)
1.00	1.9 (3)	2.72 (6)	2.6 (3)	2.34 (6)	9 (2)	11.5 (3)

[a] Analytical concentrations used: BF_4^-, $C_{Hg} \approx 0.9$–9 mM, $C_{Cu} = 0.98$ mM, $C_L \approx 0.024$ or 0.038 mM; $CF_3SO_3^-$, $C_{Hg} \approx 0.7$–7 mM, $C_{Cu} = 0.93$ or 1.85 mM, $C_L = 0.028$ or 0.078 mM; NO_3^-, $C_{Hg} \approx 1$–10 mM, $C_{Cu} = 1.0$ mM, $C_L \approx 0.038$ mM. [b] Data are somewhat scattered as indicated by the low value of the squared correlation coefficient ($r^2 = 0.79$).

data were subsequently plotted on a Hewlett-Packard Model 7047A *X*–*Y* recorder for analysis. Reactions were monitored by measuring the absorbance changes in the region of 387–390 nm, taking advantage of the intense absorption of the $Cu^{II}L$ complexes in this region ($\epsilon \approx 6000$–8000 $M^{-1}\ cm^{-1}$).[2,3]

For each series of measurements, the concentration of Hg(II) ion was varied by at least 10-fold, generally within the range of 0.5–20 mM, while the total concentration of Cu(II) was held at about 0.5–1.0 mM, both being in excess over the total ligand concentration which was in the range 0.02–0.09 mM. Due to the relatively small values for the $Cu^{II}L$ stability constants ($K_{CuL'} = 10^3$–$10^5\ M^{-1}$),[2,3] some dissociated ligand was initially present in all cases despite the addition of excess Cu(II). However, this free ligand reacted rapidly with the added Hg(II) according to reaction 7 and did not influence the pseudo-first-order kinetics as measured from the changes in the $Cu^{II}L$ absorbance. All reactions were conducted in acid solution (pH < 2.0) to prevent the formation of hydroxymercury(II) species. As previously noted, the formation and dissociation rates are independent of acid concentration since the ligands do not protonate.[4,10]

Results

The kinetics for the overall exchange process (reaction 6) involved measurable contributions from both the dissociation and Hg(II) displacement pathways (reactions 5′ and 7–9). Since Hg–S bonds are much stronger than Cu–S bonds,[12] it is presumed that, in the Hg(II) displacement pathway, the binuclear species, once formed, tends to proceed to products so that the rate of disappearance of CuL′ by this pathway is directly related to the k_1 term. This yields the following overall rate equation:

$$-d[CuL']/dt = k_d[CuL'] - k_f[Cu^{2+}][L] + k_1[Hg^{2+}][CuL'] \tag{10}$$

Application of the steady-state approximation to [L] yields the following expression:

$$-\frac{d[CuL']}{dt} = \frac{\{k_{Hg}{}^{L}k_d[Hg^{2+}] + k_1[Hg^{2+}](k_f[Cu^{2+}] + k_{Hg}{}^{L}[Hg^{2+}])\}[CuL']}{k_f[Cu^{2+}] + k_{Hg}{}^{L}[Hg^{2+}]} \tag{11}$$

In comparing the relative magnitude of the two terms in the denominator, we note that both aquated Hg^{2+} and Cu^{2+} generally undergo ligand complexation extremely rapidly.[11] For the formation of copper(II)–polythiaether complexes, however, the rate-determining step appears to be shifted to the point of second bond formation (chelate ring closure), due to the relative weakness of the first Cu–S bond, resulting in k_f values which are smaller than normal for Cu(II).[8,13] By contrast, Hg(II) forms very strong bonds to thiaether sulfur donor atoms[12] so that the rate-determining step is expected to be at the point of first bond formation. Under the conditions used in this study, where the total concentration of Hg^{2+} was about equal to or greater than that of Cu^{2+}, we conclude that $k_{Hg}{}^{L}[Hg^{2+}] \gg k_f[Cu^{2+}]$, resulting in the following simplified expression:

$$-d[CuL']/dt = \{k_d + k_1[Hg^{2+}]\}[CuL'] \tag{12}$$

Furthermore, in this study $[Hg^{2+}] \gg [CuL']$, yielding the pseudo-first-order relationship

$$-d[CuL']/dt = k_{app}[CuL'] \tag{13}$$

where

$$k_{app} = k_d + k_1[Hg^{2+}] \tag{14}$$

For each of the three ligand systems studied, the kinetic data were treated using eq 13 and the resulting k_{app} values exhibited excellent linearity when plotted according to eq 14 to yield k_d as the intercept and k_1 as the slope (Figure 3). The values for these rate constants are listed in Table I for all three ligand systems as a function of perchlorate ion concentration (0.05–1.0 M).

For Cu^{II}([14]aneS_4), additional (but more limited) studies were carried out in which ClO_4^- was replaced by BF_4^-, $CF_3SO_3^-$, or NO_3^-. The results are given in Table II. In the presence of $CF_3SO_3^-$ there was evidence of a second very fast reaction, of undetermined origin, and a similar phenomenon was apparent in the studies involving 0.10 M BF_4^- (but not with higher concen-

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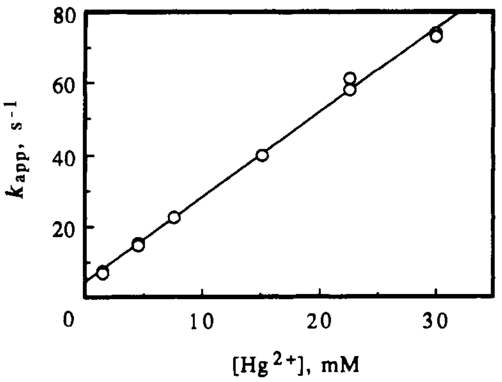

Figure 3. Typical plot of eq 14 for the apparent rate constant, k_{app}, for aquamercury(II) exchange with the $\mathrm{Cu^{II}([14]aneS_4)}$ complex as a function of Hg(II) concentration in aqueous solution at 25.0 °C: C_{Cu} = 0.551 mM, $C_L \approx 0.040$ mM, C_{Hg} = 1.5–30 mM, $[\mathrm{ClO_4^-}]$ = 0.50 M.

trations). This faster reaction was too rapid to be studied accurately, and no attempt was made to obtain rate constants.

Discussion

For all systems studied, the precision of k_d is limited by the fact that a predominant percentage of the overall reaction rate was carried by the mercury displacement pathway (reactions 8 and 9), particularly at higher concentrations of $\mathrm{Hg^{2+}}$ (see Figure 3). Nonetheless, the trends are sufficiently well established to allow reasonably quantitative conclusions to be reached concerning the nature of the anion effect upon both k_d and k_1.

Resolution of Specific Dissociation Rate Constants. Comparison of the data in Tables I and II shows a general decrease in k_d as the anion concentration is increased. The lone exception involves $\mathrm{Cu^{II}([14]aneS_4)}$ in the presence of $\mathrm{NO_3^-}$ (Table II) for which no significant trend is observed. This latter observation is consistent with our previous thermodynamic studies on the copper(II)–polythiaether complexes in which it was observed that $\mathrm{NO_3^-}$ has no effect upon the conditional stability constants whereas $\mathrm{ClO_4^-}$, $\mathrm{BF_4^-}$, and $\mathrm{CF_3SO_3^-}$ cause a dramatic increase in $K_{\mathrm{CuL}'}$.[3] Thus, we conclude that $\mathrm{NO_3^-}$ either does not form an adduct with $\mathrm{Cu^{II}([14]aneS_4)}$ or has no influence on the Cu–S bonding interactions and that the k_d values observed for the solutions containing $\mathrm{NO_3^-}$ represent the pure dissociation rate constant for $\mathrm{CuL^{2+}}$, designated as k^{CuL}.

The decrease in k_d with increasing anion concentration for each of the other series of kinetic measurements indicates that the $\mathrm{CuLX^+}$ adducts are slower to dissociate than are the corresponding aquated complex species $\mathrm{CuL^{2+}}$. Therefore, the limiting value of k_d for each system at low anion concentration should be virtually identical to the value of k_d obtained in the presence of $\mathrm{NO_3^-}$. From a qualitative standpoint, the k_d values for $\mathrm{Cu^{II}([14]aneS_4)}$ in the presence of $\mathrm{ClO_4^-}$, $\mathrm{BF_4^-}$, and $\mathrm{CF_3SO_3^-}$ appear to extrapolate to the upper range of k_d values observed in the studies using $\mathrm{NO_3^-}$.

In quantitatively resolving the dissociation rate constant trends, we have assumed that the observed k_d values can be factored into two contributing terms:

$$k_d[\mathrm{CuL}'] = k^{\mathrm{CuL}}[\mathrm{CuL^{2+}}] + k^{\mathrm{CuLX}}[\mathrm{CuLX^+}] \qquad (15)$$

This expression can then be rearranged to the form

$$k_d\alpha_{\mathrm{CuL}} = k^{\mathrm{CuL}} + k^{\mathrm{CuLX}}K_{1X}[\mathrm{X^-}] \qquad (16)$$

where α_{CuL} (as defined in accordance with Ringbom's convention)[14] is the reciprocal mole fraction of the CuL′ species which is not coordinated to the anion[2,3]

$$\alpha_{\mathrm{CuL}} = [\mathrm{CuL}']/[\mathrm{CuL^{2+}}] = 1 + K_{1X}[\mathrm{X^-}] \qquad (17)$$

and K_{1X} is the equilibrium constant for the formation of the anion adduct as defined by reaction 2.[2] Although the ionic strength varies with anion concentration, the ligand is uncharged and the pure dissociation process involves only the solvent and the complex. Thus, the influence of electrostatic effects upon the dissociation rate constants should be insignificant. As has been previously noted, however, the magnitude of K_{1X} (in concentration terms) does depend upon the ionic strength.[3] Values of K_{1X} appropriate to each ionic strength studied were calculated using the relationship[2]

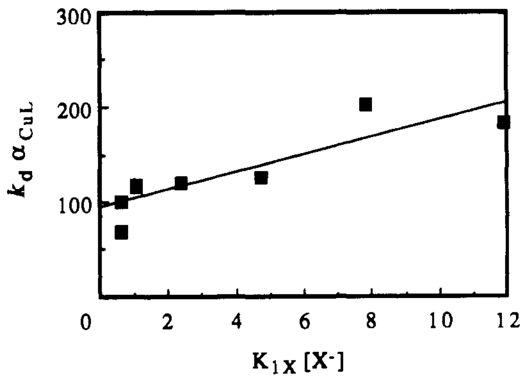

Figure 4. Typical plot of eq 16 showing the resolution of the direct dissociation rate constants for the $\mathrm{Cu([13]aneS_4)^{2+}}$ complex and the $\mathrm{Cu([13]aneS_4)X^+}$ adduct formed with perchlorate ion. In this plot, k^{CuL} is determined from the intercept and k^{CuLX} is determined from the slope.

Table III. Resolved Dissociation and Mercury(II) Displacement Rate Constant Values Obtained from Linear Regression Analysis for the $\mathrm{CuL^{2+}}$ and $\mathrm{CuLX^+}$ (Perchlorate Adduct) Species of the Copper(II)–Tetrathiaether Complexes in Aqueous Solution at 25 °C

complexed ligand	k^{CuL}, s^{-1}	k^{CuLX}, s^{-1}	$k_{\mathrm{Hg}}{}^{\mathrm{CuL}'} \times 10^{-3}$, s^{-1}	$k_{\mathrm{Hg}}{}^{\mathrm{CuLX}'} \times 10^{-3}$, s^{-1}
$\mathrm{[12]aneS_4}$	8 (2)	1.3 (4)	2.6 (3)	0.09 (6)
$\mathrm{[13]aneS_4}$	95 (11)	9 (2)	10 (1)	4 (1)
$\mathrm{[14]aneS_4}$	18 (2)	1.2 (3)	1.4 (3)	0.53 (6)

$$K_{1X} = K_{1X}{}^0(f_{\mathrm{CuL}}f_{\mathrm{X}}/f_{\mathrm{CuLX}}) \qquad (18)$$

where $K_{1X}{}^0$ represents the adduct stability constant corrected to zero ionic strength and f_{CuL}, f_{X}, and f_{CuLX} are the activity coefficients for the respective subscripted species as calculated by utilizing the empirically extended form of the Debye–Hückel equation.[15] In the case of $\mathrm{ClO_4^-}$, we have utilized our previously determined value of $K_{1X}{}^0 \approx 24$ M^{-1} (aqueous solution, 25 °C)[3] in calculating appropriate values of K_{1X} prior to plotting the k_d data using eq 16 (see Figure 4). For all three complexes studied, the resulting plots show considerable scatter, indicating that the trends are not large compared to the precision of the k_d data. Nonetheless, the intercepts and slopes are statistically significant, and the resultant values of k^{CuL} and k^{CuLX}, as determined by linear regression analysis, are given in Table III along with their calculated standard deviations.

From Table III, two general observations can be made. The resolved k^{CuL} value obtained from the $\mathrm{ClO_4^-}$ data for the $\mathrm{Cu^{II}([14]aneS_4)}$ complex (18 ± 2 s^{-1}) is within experimental error of the upper range of k_d obtained directly in the presence of $\mathrm{NO_3^-}$ (14 ± 2 s^{-1}). It is also apparent that the resolved k^{CuLX} values for the $\mathrm{ClO_4^-}$ adducts with all three complexes are about an order of magnitude smaller than the corresponding k^{CuL} values.

As noted from Table II, the trends in k_d for $\mathrm{Cu^{II}([14]aneS_4)}$ as a function of $[\mathrm{BF_4^-}]$ and $[\mathrm{CF_3SO_3^-}]$ are similar to that observed for $\mathrm{ClO_4^-}$, implying that the degree of $\mathrm{CuLX^+}$ adduct formation is similar for these three anions. Unfortunately, $K_{1X}{}^0$ has not been determined for these other anions so that eqs 18 and 16 cannot be applied rigorously.

Aqueous Formation Rate Constants. In view of the difficulty of determining the formation rate constants for the copper(II) complexes formed with the macrocyclic polythiaether ligands directly in aqueous solution, these values were previously deter-

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(14) Ringbom, A. *Complexation in Analytical Chemistry*; Wiley: New York, 1963.

(15) For specific values of the parenthetical term in eq 18, see Table V in ref 3.

Table IV. Comparison of Formation Rate Constant Values for the Copper(II)-Tetrathiaether Complexes As Calculated from the Dissociation Rate Constants and Stability Constants at Zero Anion Concentration in Aqueous Solution at 25 °C, and Previously Determined Formation Rate Constant Values in 0.10 M Perchlorate As Extrapolated to Aqueous Conditions

complexed ligand	$K_{CuL}{}^0 \times 10^{-3}$,[a] M^{-1}	$k_{Cu}{}^L \times 10^{-4}$,[b] $M^{-1}\ s^{-1}$	$k_{Cu}{}^L \times 10^{-4}$,[c] $M^{-1}\ s^{-1}$
[12]aneS$_4$	1.6 (2)	1.3 (3)	0.65
[13]aneS$_4$	1.44 (9)	14 (2)	7.4
[14]aneS$_4$	10.8 (2)	19 (2)	13

[a] Reference 3; $[ClO_4^-] \rightarrow 0$. [b] Calculated from the direct dissociation rate constant, k^{CuL}, in aqueous solution using eq 19 (this work); $[ClO_4^-] \rightarrow 0$. [c] Extrapolated to aqueous conditions from complex formation kinetic studies conducted in methanol-water mixtures (ref 8); $[ClO_4^-] = 0.1$ M.

mined indirectly by measuring the formation kinetics in a wide range of methanol-water solvent mixtures and then rigorously extrapolating the resulting formation rate constants to pure water.[8] The present results provide an alternative method for calculating the formation rate constants for aquacopper(II) ion reacting with the polythiaether ligands, $k_{Cu}{}^L$, by multiplying the resolved k^{CuL} values in Table III by the complex stability constants:

$$k_{Cu}{}^L = K_{CuL}{}^0 k^{CuL} \tag{19}$$

Since the k^{CuL} values determined in this work are presumed to apply to conditions of infinite dilution (i.e., zero concentration of anions), it is appropriate to utilize the activity stability constants, $K_{CuL}{}^0$, as previously determined in our laboratory.[3] These constants are given in Table IV along with the calculated anion-independent $k_{Cu}{}^L$ values ($\mu = 0$). Also listed in the far right column for comparison are aqueous $k_{Cu}{}^L$ values ($\mu = 0.10$ M ClO_4^-) previously extrapolated from measurements in methanol-water mixtures. The fact that the two sets of $k_{Cu}{}^L$ values are reasonably similar would appear to uphold the validity of the data in the current study. The actual difference in the two sets of formation rate constants appears to be about 2-fold for all three systems. This difference may be fortuitous, or it may actually represent a slight retardation in the formation rate constants in the presence of ClO_4^-.

Correlation of Complexation Kinetics in 80% Methanol and in Water. In our earlier analysis of the effect of ClO_4^- upon the $Cu^{II}L$ stability constants, we did not presume the formation of ClO_4^- adducts with the solvated copper(II) ion since there was no direct evidence for a CuX^+ species. However, the increase in k_f with increasing $[ClO_4^-]$ observed in 80% methanol (Figure 2) indicates that such adducts are significant, and although the k_f trend in water, if real, appears to be in the opposite direction, a consistent phenomenon may account for both trends.

It is generally recognized that $Cu(H_2O)_6^{2+}$ is extremely rapid in its substitution reactions due to the lability of the axially coordinated water molecules as a result of Jahn-Teller distortion.[11,16] The introduction of a single unique inner-sphere donor atom would remove the degeneracy of the d-orbitals and should result in much slower substitution kinetics for mixed donor species. In fact, in the case of solvated Cu^{2+} reacting with NH_3, we have previously attributed the marked decrease in formation rate constant values with increasing methanolic content to the more sluggish inner-sphere substitution kinetics of $Cu(H_2O)_5(CH_3OH)^{2+}$ for the very reason that CH_3OH decreases the Jahn-Teller distortion which normally labilizes the axial water molecules in $Cu(H_2O)_6^{2+}$.[8] The formation of $Cu(H_2O)_5X^+$ (if such a species exists to any appreciable extent) should have the same effect in influencing complex formation in aqueous solution. In 80% methanol, however, $Cu(H_2O)_5(CH_3OH)^{2+}$ is already the predominant form of solvated Cu(II)[8] and the observed kinetics of solvated Cu(II) with simple ligands appears to be carried exclusively by the small amount of $Cu(H_2O)_6^{2+}$ present due to the decreased substitutional lability of $Cu(H_2O)_5(CH_3OH)^{2+}$.[8] The introduction of an inner-sphere anion into this latter species (to form $Cu(H_2O)_4(CH_3OH)X^+$) might then result in substitutional labilization, causing this latter species to contribute significantly to the formation kinetics in this solvent mixture.

In apparent corroboration of the foregoing rationale, we note that a recent study by Izatt, Gellman, and co-workers on related Cu(II)-tetrathiaether complexes has revealed that the effect of ClO_4^- on stabilizing the $Cu^{II}L$ stability constants is magnified in 80% methanol relative to water.[7] This observation indicates that ClO_4^- either increases the formation rate constants in the methanolic solvents or causes a greater decrease in the dissociation rate constants than is the case in water, or both (as suggested by Figure 2).

Resolution of Specific Mercury(II) Displacement Rate Constants. The mercury(II) ion displacement kinetics provide independent evidence for the effects caused by the formation of anion adducts. Since we have already concluded that NO_3^- does not form anion adducts (or, at any rate, does not influence inner-sphere substitution rates), the significant increase in k_1 observed for the $Cu^{II}([14]aneS_4)$ system as $[NO_3^-]$ is increased (Table II) must be attributed to the influence of *increasing ionic strength* upon the displacement pathway in facilitating the approach of the two positively charged reactants. The failure of k_1 to show similar increasing trends in the presence of ClO_4^-, $CF_3SO_3^-$, and BF_4^- (Tables I and II) must then be attributable to a counterbalancing trend such as the slower displacement of $Hg_{aq}{}^{2+}$ with the $CuLX^+$ species compared to the CuL^{2+} species.

The observed displacement rate constants can presumably be expressed in a form parallel to that shown for the direct dissociation in eq 15, viz.

$$k_1[Hg^{2+}][CuL'] = k_{Hg}{}^{CuL}[Hg^{2+}][CuL^{2+}] + k_{Hg}{}^{CuLX}[Hg^{2+}][CuLX^+] \tag{20}$$

or

$$k_1\alpha_{CuL} = k_{Hg}{}^{CuL} + k_{Hg}{}^{CuLX}K_{1X}[X^-] \tag{21}$$

Despite the linear appearance of eq 21, $k_{Hg}{}^{CuL}$ and $k_{Hg}{}^{CuLX}$ are not expected to be constant with changing ionic strength due to the electrostatic interactions between the Hg(II) ion and the Cu(II) complex. Moreover, since the charges associated with CuL^{2+} and $CuLX^+$ are not identical, the value for the formation of the precursor outer-sphere complex, K_{os}, will differ for the two specific rate constants. This can be factored out of each term in the following manner:

$$k_1\alpha_{CuL} = K_{os(CuL)}k_{Hg}{}^{CuL'} + K_{os(CuLX)}k_{Hg}{}^{CuLX'}K_{1X}[X^-]$$

or, upon rearranging

$$\frac{k_1\alpha_{CuL}}{K_{os(CuL)}} = k_{Hg}{}^{CuL'} + \frac{K_{os(CuLX)}K_{1X}[X^-]}{K_{os(CuL)}}k_{Hg}{}^{CuL'} \tag{22}$$

where $K_{os(CuL)}$ and $K_{os(CuLX)}$ represent the outer-sphere equilibrium constants involving Hg(II) interacting with CuL^{2+} and $CuLX^+$, respectively, and the primed rate constants represent the subsequent first-order displacement reactions following the formation of the bimolecular outer-sphere complexes (e.g., $k_{Hg}{}^{CuL'} = k_{Hg}{}^{CuL}/K_{os(CuL)}$).

Calculation of $K_{os(CuL)}$ and $K_{os(CuLX)}$ can be made using the general expression[17]

$$K_{os} = {}^4\!/_3\pi N_A a^3\left\{10^{-3}\exp\left[-\frac{Z_A Z_B e_0{}^2}{Dk_BT}\left(\frac{1}{a'} - \frac{\kappa}{1+\kappa a'}\right) + 2.303b\mu\right]\right\} \tag{23}$$

where N_A represents Avogadro's number, a is the reaction cross-section (cm) (i.e., the sum of the effective collisional radii

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(16) Sokol, L. S. W. L.; Fink, T. D.; Rorabacher, D. B. *Inorg. Chem.* **1980**, *19*, 1263-1266.

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

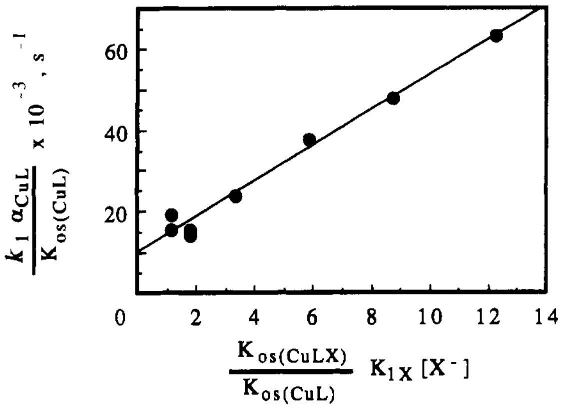

Figure 5. Example plot of eq 22 showing the resolution of the mercury(II) displacement rate constants with the $Cu([13]aneS_4)^{2+}$ complex and the $Cu([13]aneS_4)X^+$ adduct formed with perchlorate ion. In this plot, $k_{Hg}{}^{CuL'}$ is determined from the intercept and $k_{Hg}{}^{CuLX'}$ is determined from the slope.

of the two reactant species $Hg_{aq}{}^{2+}$ and CuL^{2+} or $CuLX^+$), Z_A and Z_B are the formal charges on the two reactants, e_0 is the electronic charge (esu), D is the solvent dielectric constant, k_B is the Boltzmann constant (erg K^{-1} mol^{-1}), a' is the distance between the charge centers in the reactive outer-sphere complex (cm), κ is the reciprocal radius of the ionic atmosphere as calculated from the relationship

$$\kappa = (8\pi N_A e_0{}^2\mu/1000Dk_BT)^{1/2} \qquad (24)$$

μ is the ionic strength of the solution, and the parameter b in eq 23 is an empirical correction term which becomes significant at higher ionic strength ($\mu > \sim 0.2$).

Application of the foregoing calculations is impeded in the case of the displacement reaction data both by uncertainties in the nature of the $Cu^{II}L$ complex at the time of the formation of the effective outer-sphere complex and by the relatively large ionic strengths involved in this study. The choice of the appropriate a and a' values is somewhat arbitrary. On the basis of molecular models, it appears that a' is in the range of 10–12 Å and, to a first approximation, the same value can be utilized for a.[18]

The best experimentally determined value for b is -0.089, as measured for HCl in aqueous solution at 25 °C.[19] Although this empirical parameter is expected to depend upon the charges of the interacting species, the specific dependence has never been definitively established. Davies has suggested that this parameter varies as the charge product,[20] which would yield a value of $b = -0.36$ for Hg^{2+} reacting with CuL^{2+}. On the basis of this value and $a = a' = 10$ Å, the ratio $k_1/K_{os(CuL)}$ was found to decrease steadily from 7.8×10^3 to $3.6 \times 10^3\ s^{-1}$ for $Cu^{II}([14]aneS_4)$ as $[NO_3{}^-]$ increased—whereas eq 22 predicts that this ratio should be a constant (representing $k_{Hg}{}^{CuL'}$) in the absence of $CuLX^+$ adduct formation. The $k_1/K_{os(CuL)}$ ratio can be made constant (within experimental error), however, either by maintaining $a' = 10$ Å and decreasing b to zero (yielding $k_{Hg}{}^{CuL'} \approx 8 \times 10^3\ s^{-1}$) or by increasing a' to 12 Å (still considered to be a reasonable value on the basis of molecular models)[18] and setting $b = 0.18$ (yielding $k_{Hg}{}^{CuL'} = 3 \times 10^3\ s^{-1}$). The latter set of parameters is much more acceptable, and we have utilized these values (i.e., $a = a' = 12 \times 10^{-8}$ cm with $b = 0.18$ for $K_{os(CuL)}$ and $b = 0.09$ for $K_{os(CuLX)}$) in treating the displacement kinetic data in the presence of the other anions.

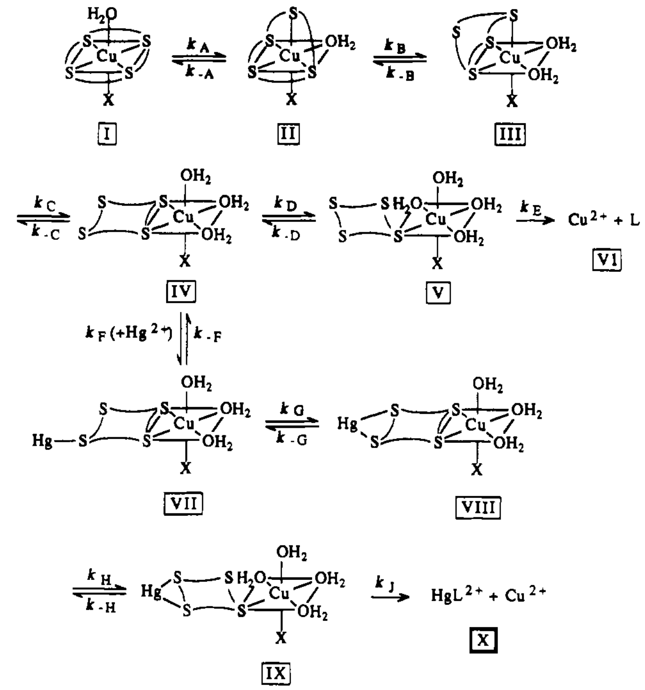

Figure 6. Schematic mechanism showing the proposed stepwise dissociation pathway of the $CuLX^+$ complex (designated by rate constants k_A, k_B, k_C, k_D, and k_E) and the displacement pathway involving the attachment of the Hg(II) ion to the partially dissociated Cu(II) complex (k_F, k_G, k_H, and k_J). For both pathways, it is suggested that the major influence of the coordinated anion X^- may be in reducing the magnitude of the rate constants for Cu–S bond rupture (k_B, k_C, k_D, k_E, k_H, and k_J), the first two of these being common to both reaction pathways.

Using the parameters noted above, we have plotted the k_1 values for all three perchlorate studies according to eq 22. This treatment yields good linearity as illustrated by the plot of the $Cu^{II}([13]aneS_4)$ data as shown in Figure 5. The resolved values for the first-order displacement rate constants (following the formation of the outer-sphere complex) for both the CuL^{2+} and $CuLX^+$ species for all three systems are included in Table III. Due to the uncertainties in the computation of the K_{os} values, the absolute magnitudes of the resolved $k_{Hg}{}^{CuL'}$ and $k_{Hg}{}^{CuLX'}$ constants may be in error, and caution should be exercised in drawing rigorous conclusions regarding these values. However, the relative magnitudes of these rate constants (which could also be generated by dividing the $NO_3{}^-$ k_1 values into the k_1 values obtained in the presence of the other anions) should have significance. It is noted for all three ligand systems that the values of $k_{Hg}{}^{CuL'}$ are larger than those of $k_{Hg}{}^{CuLX'}$, indicating once again that the anion adduct retards dissociation. For the $Cu^{II}([12]aneS_4)$ system, the ratio of these two resolved rate constants is especially large, suggesting that it is difficult for the $Cu^{II}([12]aneS_4)$ complex to incorporate simultaneously both the anion and the Hg(II) ion in a mixed complex. In view of the apparent rigidity of the $[12]aneS_4$ ligand,[8] this behavior is not surprising.

For all three ligand systems, the $k_{Hg}{}^{CuL'}$ values listed in Table III are approximately 2 orders of magnitude larger than the corresponding k^{CuL} values. Since both sets of values represent first-order rate constants, this comparison is a valid one and represents the degree to which Hg(II) promotes the dissociation process.

Proposed Mechanistic Role of Anions. The proposed stepwise mechanism for $CuLX^+$ reacting by both pathways is illustrated in Figure 6. In our earlier analysis of the mechanism for Cu(II)–macrocyclic tetrathiaether complex formation,[8] it was concluded that the formation of the second Cu–S bond (i.e., closure of the first chelate ring) represents the rate-determining step. Thus, it follows that the rupture of the next to last Cu–S bond

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(18) If two Cu–S bonds are ruptured at the point of outer-sphere complex formation, molecular models suggest that the value of a' may be approximately 10–12 Å. By contrast, the value of a may be considered to have a substantially smaller value if one views the $Cu^{II}L$ unit as a "donor atom with an appended tail" (see, e.g., ref 17), but this latter consideration is presumably offset by the fact that only a fraction of the partially dissociated $Cu^{II}L$ species may be in a conformation suitable to promote further reaction. It should be noted that the a^3 term and any statistical correction terms will affect only the preexponential factor in eq 23 and, thus, will be uniform for all conditions studied, affecting both $K_{os(CuL)}$ and $K_{os(CuLX)}$ equally. Only the exponential term in eq 23 affects the trends in k_1 as a function of ionic strength.

(19) See Table IV in ref 17.

(20) Davies, C. W. *J. Chem. Soc.* **1938**, 2093–2098.

(represented by rate constant k_D in Figure 6) represents the rate-determining step in the direct dissociation process. For $Cu^{II}([14]aneS_4)$, the ligand must first invert a sulfur donor atom and rearrange into a folded complex (species II),[8,21] following which the Cu–S bonds must be ruptured sequentially (steps k_B, k_C, k_D, and k_E). Although the role of the anion in retarding the dissociation process is not entirely clear, two possibilities would appear to exist: (i) an axially coordinated anion may affect the strength of the Cu–S bonds through inner-sphere effects, slowing the Cu–S bond ruptures, or (ii) the rearrangement required to place one of the macrocyclic ligand donor atoms into an axial site (species II in Figure 6) may be impeded by an interacting coordinated anion. However, we note that both $Cu^{II}([12]aneS_4)$ and $Cu^{II}([13]aneS_4)$ are initially square pyramidal[6] and should not require the "folding" step prior to commencing Cu–S bond rupture. (Moreover, in our earlier stability constant studies,[3] ClO_4^- also stabilized an acyclic Cu(II)–tetrathiaether complex in which no folding is required.) On the basis of the similar kinetic behavior observed for all three systems included in this study, we conclude that the anion effect is most probably manifested as an inner-sphere effect upon the Cu–S bond rupture rates.

In considering the general mechanism of metal displacement reactions,[11] it is probable that two Cu–S bonds must rupture before an effective mixed metal complex can be formed (species VII in Figure 6). Since it is unlikely that both bond ruptures will occur within the lifetime of an outer-sphere complex, the effective reaction pathway is believed to involve the collision of the Hg_{aq}^{2+} species with a partially dissociated CuL^{2+} complex to form the reactive outer-sphere complex. The intermediate CuLHg′ species which must then be formed is expected to involve each metal ion bonded to two adjacent S donor atoms (species VIII), analogous to the structure observed crystallographically by Moore and coworkers[22] for the binuclear complex $Hg_2([14]aneS_4)Cl_4$. The sequential rupture of Hg(II)–OH_2 bonds and formation of Hg(II)–S bonds (steps k_F and k_G) to generate species VIII should be extremely rapid, and it is likely that the rate-determining step for this pathway is again represented by the rupture of the next to last Cu–S bond (step k_H). Thus, the Hg(II) ion undoubtedly facilitates displacement of the Cu(II) ion by blocking the reformation of the Cu–S bonds which have undergone dissociation prior to the mercury attachment. The role of the anion in influencing the dissociation of the first two Cu–S bonds could then be essentially the same for the mercury displacement pathway and for the unaided dissociation pathway.

In the current work we have confirmed the fact that nitrate is the only anion, of those tested, which does not interact with the CuL^{2+} complexes. We note two distinct differences between this anion and the other anions tested: (i) NO_3^- is a planar species whereas ClO_4^-, $CF_3SO_3^-$, and BF_4^- are essentially tetrahedral, and (ii) NO_3^- is the only species to involve resonance which may result in a "softening" of the oxygen donor atoms. Since it is difficult to conceive of a process whereby the differences in anion geometry could account for the observed contrast in kinetic behavior, we conclude that the differing effect of NO_3^- is attributable to the difference in the relative electronic interactions of the oxygen donor atoms with either the solvent (in increasing the strength of anion solvation and, thereby, decreasing CuX^+ formation) or with the Cu(II) ion once it is coordinated.

Conclusions

The similar behavior of ClO_4^-, $CF_3SO_3^-$, and BF_4^- in decreasing the rate constants of both the unaided $Cu^{II}L$ dissociation and the mercury(II) displacement pathways is consistent with the supposition that the anion is interacting directly with the Cu(II) ion and that this interaction, in turn, decreases the rate of Cu–S bond rupture. This latter phenomenon is then manifested as an increase in the observed stability constants of the $Cu([n]aneS_4)$ species as previously reported.[2,3,7]

The proposed influence of the coordinated anions upon the properties of the Cu–S bonds further suggests that the subsequent chemical and physical properties of the CuL^{2+} and $CuLX^+$ species may differ in some aspects. Therefore, it is recommended that, in probing the relative properties of $Cu^{II}L$ complexes, investigators should attempt to resolve the individual behavior attributable to each of these two species. In the absence of such data, it should be recognized that reported properties may represent the composite behavior of the CuL^{2+} and $CuLX^+$ species and that the apparent properties may change with changing anions.

On the basis of the observed results with NO_3^-, it is apparent that NO_3^- could be used to maintain a constant ionic strength while the concentration of the adduct-forming anions is varied in order to simplify the resolution of the two individual rate constant terms in eq 22 (since this would eliminate the need to make corrections for ionic strength effects). Moreover, the exclusive use of nitrate salts may circumvent the problem associated with the formation of anion adducts altogether. However, this approach should be used with caution since, as we have noted earlier,[3] the addition of large amounts of NO_3^- results in the apparent oxidation of the polythiaether ligands, particularly in highly acidic media.

Note Added in Proof. It has come to our attention that Anderson and Shain reported the reduction of hexaaquocopper(II) ion at a mercury electrode occurs much more rapidly in mixed nitrate–perchlorate solutions than in solutions containing nitrate alone, a phenomenon which they attributed to the effect of nitrate on the double-layer (Anderson, J. L.; Shain, I. *Anal. Chem.* **1978**, *50*, 163–171). In light of the current work, however, their experimental observations would appear to be more logically interpreted in terms of perchlorate adduct formation with the aquocopper(II) ion rather than any effect attributable to the nitrate ion. If perchlorate does interact with aquocopper(II) ion, the value for perchlorate adduct formation with the $Cu^{II}L$ species must be even greater than the values which we have previously assigned assuming no Cu(II)(aq) adducts.[2,3]

Acknowledgment. This work was supported, in part, by the National Institute of General Medical Sciences.

Registry No. $Cu[12]aneS_4^{2+}$, 57673-84-4; $Cu[12]aneS_4(ClO_4)^+$, 140873-96-7; $Cu[13]aneS_4^{2+}$, 57673-85-5; $Cu[13]aneS_4(ClO_4)^+$, 140873-97-8; $Cu[14]aneS_4^{2+}$, 57673-86-6; $Cu[14]aneS_4(ClO_4)^+$, 140873-98-9; Hg(II), 14302-87-5.

Supplementary Material Available: Tables of experimental rate constants for 363 individual kinetic runs (9 pages). Ordering information is given on any current masthead page.

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(21) Crystal structures for $Cu^{II}([12]aneS_4)$ and $Cu^{II}([13]aneS_4)$ indicate that, due to the smaller cavity size, the Cu(II) atom sits above the plane of the four sulfur donor atoms, resulting in a square-pyramidal complex (ref 6). As a result, prior folding may not be essential in the dissociation of these two complexes.

(22) Alcock, N. W.; Herron, N.; Moore, P. *J. Chem. Soc., Dalton Trans.* **1978**, 394–399.