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Characterization of Perchlorate Adduct Formation with Copper(II)–Cyclic Polythia Ether Complexes and Determination of Corrected Stability Constants

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The conditional stability constants for the complexes formed between Cu(II) and several cyclic polythia ether ligands have been determined spectrophotometrically in the presence of perchlorate ion concentrations of 0.010, 0.025, 0.050, 0.10, 0.25, 0.50, and 1.00 M at 5, 15, 25, and 35 °C. The data indicate that the Cu(II) complexes formed with [12]aneS₄, [13]aneS₄, and [16]aneS₄ increase in apparent stability with increasing perchlorate as was earlier observed for Cu^{II}([14]aneS₄). By contrast, the conditional stability constant of Cu^{II}([15]aneS₅), the only pentathia ether complex studied, is virtually unaffected by varying perchlorate. The data for the tetrathia ether complexes can be interpreted as indicative of the formation of a 1:1 adduct with the perchlorate anion. A linear mathematical expression is developed to permit the resolution of the thermodynamic stability constant, K_{CuL}° , for the Cu(II)–tetrathia ether complexes extrapolated to zero ionic strength. This mathematical treatment also yields values of an apparent equilibrium constant, K_{iX}° , representing the interaction of a perchlorate ion with the Cu(II)–tetrathia ether complexes (i.e., for the reaction $CuL^{2+} + X^- \rightleftharpoons CuLX^+$). The resultant thermodynamic parameters characteristic of these two equilibrium constants and the activity-corrected 25 °C equilibrium constant values for each system are as follows (ΔH_{iX}° , ΔS_{iX}° , K_{iX}° for 25 °C, ΔH_{CuL}° , ΔS_{CuL}° , K_{CuL}° for 25 °C): for Cu^{II}([12]aneS₄), $-0.2 (\pm 1.5)$ kcal mol⁻¹, $5 (\pm 5)$ cal K⁻¹ mol⁻¹, $24 (\pm 3)$ M⁻¹, $-0.6 (\pm 1.0)$ kcal mol⁻¹, $13 (\pm 4)$ cal K⁻¹ mol⁻¹, $1.6 (\pm 0.2) \times 10^3$ M⁻¹; for Cu^{II}([13]aneS₄), $-1.8 (\pm 0.5)$ kcal mol⁻¹, $-0.2 (\pm 1.7)$ cal K⁻¹ mol⁻¹, $19 (\pm 1)$ M⁻¹, $-1.5 (\pm 0.3)$ kcal mol⁻¹, $9.4 (\pm 1.0)$ cal K⁻¹ mol⁻¹, $1.44 (\pm 0.09) \times 10^3$ M⁻¹; for Cu^{II}([14]aneS₄), $-1.7 (\pm 0.1)$ kcal mol⁻¹, $0.6 (\pm 0.4)$ cal K⁻¹ mol⁻¹, $24.2 (\pm 0.5)$ M⁻¹, $-3.1 (\pm 0.2)$ kcal mol⁻¹, $7.9 (\pm 0.5)$ cal K⁻¹ mol⁻¹, $1.08 (\pm 0.02) \times 10^4$ M⁻¹; for Cu^{II}([15]aneS₅), no estimate, no estimate, 0 M⁻¹, $-2.9 (\pm 0.2)$ kcal mol⁻¹, $8.6 (\pm 0.6)$ cal K⁻¹ mol⁻¹, $1.02 (\pm 0.08) \times 10^4$ M⁻¹; for Cu^{II}([16]aneS₄), $K_{iX}^{\circ} \approx 1 \times 10$ M⁻¹, $K_{CuL}^{\circ} \approx 1.2 \times 10^2$ M⁻¹.

Introduction

In recent years we have conducted extensive investigations into various aspects of the chemical behavior of copper(II) complexes formed with macrocyclic polythia ethers, particularly as related to structural constraints.²⁻⁷ Most of these studies have been carried out in aqueous solutions where the complexes are relatively weak ($K_{CuL} < 10^5$ M⁻¹) such that the copper(II) complexes tend to be only partially formed. Since the free ligands also exhibit very limited solubility in water ($S \leq 10^{-5}$ M), experimentation is generally restricted to very dilute solutions, which further limits the extent of complex formation. Therefore, to analyze the properties of these solutions it is necessary to determine the actual amount of complex present under a given set of conditions.

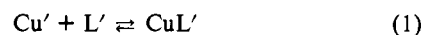
Previously, we reported on the determination of the stability constants for a series of eight polythia ether complexes formed with copper(II).⁸ The stability constant values were determined at each of four temperatures by means of a spectrophotometric method, taking advantage of the intense visible S → Cu charge-transfer bands, which are characteristic of these complexes.⁴ In the process of carrying out these studies, we noted that the intensity of the visible spectra is significantly enhanced upon the addition of several electrolytes that are generally considered to be "noncomplexing".

An example of this spectral enhancement is illustrated in Figure 1 for the addition of NaClO₄ to a solution containing a mixture of Cu(ClO₄)₂ and 1,4,8,11-tetrathiacyclotetradecane ([14]aneS₄). The positions of the two peaks at 390 and 570 nm do not appear to shift, but the absorbance increases uniformly throughout the entire visible region. Identical behavior is observed upon the

addition of HClO₄, and similar results are obtained upon addition of HBF₄, CF₃SO₃H, or their salts. Thus, it is apparent that this phenomenon is not restricted to the influence of a single cation or anion.

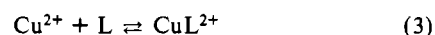
The absence of any shifts in the positions of the absorbance maxima would appear to rule out the formation of any uniquely different species. The overall appearance and chemical behavior of these solutions suggest simply that the extent of copper(II)–ligand complex formation is increased upon addition of these electrolytes. However, since the ligands are uncharged, the effect of ionic strength upon complex formation should be small and activity coefficient corrections cannot account for the observed changes in Figure 1.⁹

In the earlier stability constant study,⁸ an attempt was made to determine the variation in the apparent complex formation constant for Cu^{II}([14]aneS₄) (the most easily studied species) as a function of perchlorate ion concentration (in the form of HClO₄). Since the exact identities of the species in solution were not known, these equilibria were treated in terms of a conditional stability constant, K_{CuL}' , as defined for



$$K_{CuL}' = \frac{[CuL']}{[Cu'][L']} \quad (2)$$

where Cu' and L' represent all forms of the "free" copper ion and "free" ligand (other than that tied up as the complex) and CuL' represents all forms of the copper complex. The resultant variations in the K_{CuL}' value for Cu^{II}([14]aneS₄) were then interpreted in terms of the formation of one or two perchlorate adducts as defined by reactions 4 and 5 where X⁻ represents the perchlorate anion.



Whether the perchlorate ion is occupying an inner- or outer-sphere site in these adducts or whether, in fact, a totally different

- (1) (a) Wayne State University. (b) University of Wisconsin—Eau Claire.
- (2) Rorabacher, D. B.; Martin, M. J.; Koeningbauer, 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.
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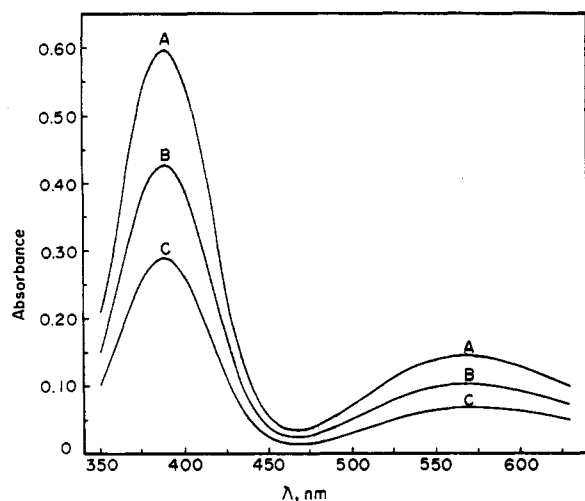


Figure 1. Effect of increasing NaClO_4 concentration upon the visible absorption spectrum of $\text{Cu}^{\text{II}}([\text{14}]\text{aneS}_4)$. All three solutions contain $5.20 \times 10^{-5} \text{ M Cu}(\text{ClO}_4)_2$ and $1.01 \times 10^{-5} \text{ M [14]aneS}_4$ with NaClO_4 concentrations for solutions A, B, and C adjusted to 0.50, 0.10, and 0.01 M, respectively. The percentages of complex formation indicated by these spectra are 74, 53, and 36%, respectively, for solutions A, B, and C.

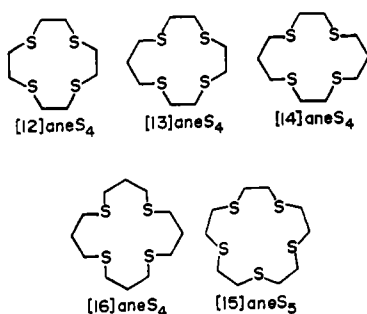


Figure 2. Ligands included in this work.

phenomenon is involved could not be determined on the basis of this single system. In order to characterize the perchlorate interaction more fully we have proceeded to determine the conditional stability constants for some related copper(II)-polythia ether complexes as a function of HClO_4 concentration. Since the polythia ether ligands do not protonate, these systems are presumed to be independent of pH and, in fact, the results can be duplicated by utilizing a perchlorate salt.

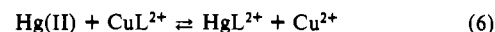
The complexing ligands studied in this work include three additional cyclic tetrathia ethers and a cyclic pentathia ether, viz. 1,4,7,10-tetrathia-cyclododecane ($[\text{12}] \text{aneS}_4$), 1,4,7,10-tetrathia-cyclotridecane ($[\text{13}] \text{aneS}_4$), 1,5,9,13-tetrathia-cyclohexadecane ($[\text{16}] \text{aneS}_4$), and 1,4,7,10,13-pentathia-cyclopentadecane ($[\text{15}] \text{aneS}_5$). These ligands are illustrated in Figure 2.

The copper(II) complexes of these four ligands are significantly weaker than the $[\text{14}] \text{aneS}_4$ complex previously studied, and the aqueous ligand solubilities are generally smaller. As a result, the stability constant data are less accurate, particularly at low perchlorate concentrations where the $K_{\text{CuL}'}$ values are smaller and the upper range of $\text{Cu}(\text{ClO}_4)_2$ concentrations that can be utilized is severely restricted by the limiting level of perchlorate ion. Nonetheless, these data shed additional light on the nature of the observed perchlorate effect and suggest that such effects must be taken into account in many other studies.

Experimental Section

Reagents. Preparation and purification of $\text{Cu}(\text{ClO}_4)_2$ and the several polythia ether ligands have been previously described.⁷ A stock $\text{Cu}(\text{II})$ solution was prepared by dissolving a weighed amount of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in distilled, deionized water, diluting to volume, and standardizing by titration with EDTA and murexide indicator. Stock $\text{Cu}(\text{II})$ -polythia ether solutions were prepared by adding a weighed sample of the appropriate solid polythia ether compound to a measured aliquot of the stock $\text{Cu}(\text{II})$ solution. This solution was stirred overnight, filtered with

a coarse- or medium-frit sintered-glass filter, and diluted to volume. The total dissolved ligand in each solution was determined by titrating it against a measured aliquot of a standard $\text{Hg}(\text{II})$ solution according to the displacement reaction



by using an Orion Research Model 901 microprocessor "Tonalizer" equipped with a Reilly mercury-pool indicating electrode. [Note: To obtain sharper potentiometric breaks at the equivalence point, it is advisable to place the aliquot of $\text{Hg}(\text{II})$ solution in the titration vessel and add the $\text{Cu}^{\text{II}}\text{L}$ solution from the buret. This approach appears to minimize adsorption of the polythia ether ligand on the mercury electrode surface.] Fresh triply distilled mercury was used for each titration.

Spectrophotometric Measurements. For each series of spectrophotometric measurements, variable aliquots of the $\text{Cu}(\text{II})$ stock solution were added to constant aliquots of the $\text{Cu}^{\text{II}}\text{L}$ stock solution and diluted to volume after the addition of HClO_4 sufficient to adjust the total perchlorate ion concentration to the desired value. For each ligand, the same series of solutions was used for absorbance measurements at 5, 15, 25, and 35 °C. Corrections for temperature-induced volume changes proved to be insignificant within the precision of the spectrophotometric measurements. All absorbance measurements were made by using a Cary Model 17D recording spectrophotometer equipped with a custom-fitted thermally jacketed cell holder with which the sides of the 5- or 10-cm cylindrical cuvettes were in direct contact. The temperature of the $\text{Cu}^{\text{II}}\text{L}$ solutions was monitored by inserting the probe of a Yellow Springs Instruments No. 44105 precision thermistor directly into the cuvette. In this manner, the temperature was controlled to within ± 0.1 °C. Maximum sensitivity was obtained by selecting the $\text{S}(\sigma) \rightarrow \text{Cu}$ charge-transfer peak in the vicinity of 400 nm ($\epsilon \sim 6000\text{--}10000 \text{ M}^{-1} \text{ cm}^{-1}$) for all absorbance measurements.

Results

As noted in the Introduction and illustrated in Figure 1, the visible spectra of the $\text{Cu}(\text{II})$ -polythia ether solutions show no alteration upon the addition of ClO_4^- other than a general increase in absorbance which is attributable to a shift of reaction 1 to the right. In fact, once a complex is fully formed, no further changes in solution absorbance are observed when perchlorate is added. These observations are interpreted to indicate that the interaction of perchlorate with these complexes has no significant influence on the $\text{S} \rightarrow \text{Cu}$ charge-transfer bands that account for the predominant peaks in the visible spectra. Thus, if perchlorate adducts are formed as suggested previously⁸ (reactions 4 and 5), the molar absorptivity values for CuL^{2+} , CuLX^+ , and CuLX_2 are identical at all visible wavelengths. Under these circumstances, the measured absorbance, A , at any selected wavelength may be correlated directly to the total amount of complex formed according to the Beer-Lambert relationship

$$A = \epsilon_{\text{CuL}'} b [\text{CuL}'] \quad (7)$$

where $\epsilon_{\text{CuL}'}$ is the apparent molar absorptivity of the total CuL' species and b represents the path length (in cm) of the spectrophotometric cell. The conditional stability constants of the $\text{Cu}^{\text{II}}\text{L}$ species included in this study were generally too small to allow reaction 1 to proceed to completion. Thus, both $\epsilon_{\text{CuL}'}$ and $[\text{CuL}']$ must be treated as unknowns. By defining the analytical concentrations of $\text{Cu}(\text{II})$ and ligand as C_{Cu} and C_{L} , respectively

$$C_{\text{Cu}} = [\text{Cu}'] + [\text{CuL}'] \quad (8)$$

$$C_{\text{L}} = [\text{L}'] + [\text{CuL}'] \quad (9)$$

and operating under conditions where $C_{\text{Cu}} \gg C_{\text{L}}$ (such that $C_{\text{Cu}} \approx [\text{Cu}']$), we can combine eq 7-9 with eq 2 and rearrange them to yield the linear relationship of McConnell and Davidson:¹⁰

$$\frac{bC_{\text{L}}}{A} = \frac{1}{\epsilon_{\text{CuL}'}} + \frac{1}{\epsilon_{\text{CuL}'} K_{\text{CuL}'} C_{\text{Cu}}} \quad (10)$$

By plotting bC_{L}/A against $1/C_{\text{Cu}}$ for a series of solutions at constant temperature and perchlorate ion concentration, the value of $\epsilon_{\text{CuL}'}$ is obtained as the reciprocal intercept and $K_{\text{CuL}'}$ as the

(10) McConnell, H.; Davidson, N. *J. Am. Chem. Soc.* **1950**, *72*, 3164-3167. The spectrophotometric method described was initially reported by: Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703-2707.

Table I. Conditional Stability Constants and Molar Absorptivity Values for the $\text{Cu}^{\text{II}}([\text{12}] \text{aneS}_4)$ Complex in Aqueous Solution as a Function of Perchlorate Ion Concentration and Temperature ($\lambda = 387 \text{ nm}$)^a

param	T, °C	[ClO ₄] ⁻ , M						
		0.010	0.025	0.050	0.10	0.25	0.50	1.0
$10^{-3}\epsilon'$, M ⁻¹ cm ⁻¹	5	8.29 (23)	7.46 (18)	6.90 (13)	7.12 (13)	6.11 (1)	7.30 (1)	7.60 (1)
	15	7.68 (20)	6.92 (8)	6.86 (11)	7.09 (11)	6.02 (1)	7.12 (1)	7.49 (1)
	25	7.39 (16)	6.88 (13)	6.84 (5)	6.87 (5)	5.86 (1)	7.00 (1)	7.32 (1)
	35	7.51 (16)	6.73 (11)	6.62 (14)	6.59 (9)	5.74 (1)	6.86 (2)	7.15 (1)
$10^{-3}K_{\text{CuL}}'$, M ⁻¹	5	2.48 (16)	2.71 (6)	6.47 (260)	3.57 (22)	5.75 (11)	9.82 (27)	28.7 (11)
	15	3.10 (21)	2.55 (14)	4.28 (101)	3.17 (16)	5.52 (12)	10.0 (2)	21.4 (12)
	25	2.33 (11)	2.02 (13)	2.45 (16)	3.01 (7)	5.67 (8)	9.18 (33)	21.9 (7)
	35	2.40 (11)	2.34 (15)	4.07 (119)	3.22 (15)	5.26 (6)	8.15 (41)	19.5 (7)
ΔH° , kcal mol ⁻¹	25	-0.63 (112)	-0.84 (10)	-0.30 (50)	-0.60 (50)	-0.41 (23)	-1.12 (42)	-1.92 (69)
ΔS° , cal K ⁻¹ mol ⁻¹		13.4 (39)	12.7 (3)	15.1 (17)	14.0 (7)	15.7 (8)	14.3 (14)	13.4 (94)

^aIn this and the following tables, the values in parentheses represent the standard deviations in terms of the final digits listed for the accompanying experimental values as determined by linear regression analysis.

Table II. Conditional Stability Constants and Molar Absorptivity Values for the $\text{Cu}^{\text{II}}([\text{13}] \text{aneS}_4)$ Complex in Aqueous Solution as a Function of Perchlorate Ion Concentration and Temperature ($\lambda = 390 \text{ nm}$)

param	T, °C	[ClO ₄] ⁻ , M						
		0.010	0.025	0.050	0.10	0.25	0.50	1.0
$10^{-3}\epsilon'$, M ⁻¹ cm ⁻¹	5	6.00 (3)	7.05 (3)	7.06 (2)	6.24 (2)	6.53 (1)	6.54 (1)	6.98 (1)
	15	5.91 (6)	6.94 (2)	6.96 (1)	6.13 (3)	6.42 (1)	6.45 (1)	6.85 (1)
	25	5.81 (16)	6.83 (2)	6.90 (3)	6.07 (2)	6.32 (1)	6.36 (1)	6.78 (1)
	35	5.77 (7)	6.73 (3)	6.75 (1)	5.95 (2)	6.20 (1)	6.20 (1)	6.57 (1)
$10^{-3}K_{\text{CuL}}'$, M ⁻¹ cm ⁻¹	5	2.14 (2)	2.42 (3)	2.86 (3)	3.36 (10)	5.48 (6)	10.6 (2)	32.6 (27)
	15	1.83 (3)	2.18 (2)	2.51 (2)	2.96 (9)	4.70 (7)	8.32 (11)	25.4 (18)
	25	1.71 (7)	1.91 (2)	2.24 (3)	2.59 (5)	3.95 (4)	6.97 (12)	17.7 (7)
	35	1.50 (3)	1.67 (2)	1.94 (1)	2.17 (3)	3.39 (4)	5.94 (4)	14.2 (5)
ΔH° , kcal mol ⁻¹	25	-1.92 (18)	-2.14 (12)	-2.19 (10)	-2.54 (13)	-2.75 (8)	-3.27 (16)	-4.87 (30)
ΔS° , cal K ⁻¹ mol ⁻¹		8.3 (63)	7.82 (41)	7.97 (35)	7.03 (44)	7.23 (27)	6.63 (56)	3.17 (103)

Table III. Conditional Stability Constants and Molar Absorptivity Values for the $\text{Cu}^{\text{II}}([\text{16}] \text{aneS}_4)$ Complex in Aqueous Solution as a Function of Perchlorate Ion Concentration and Temperature ($\lambda = 440 \text{ nm}$)

param	T, °C	[ClO ₄] ⁻ , M		
		0.010	0.10	1.0
$10^{-3}\epsilon'$, M ⁻¹ cm ⁻¹	5	15.5 (44)	9.35 (32)	7.20 (9)
	15	9.12 (460)	8.87 (26)	6.87 (6)
	25		8.24 (20)	6.80 (10)
	35		7.93 (12)	6.44 (8)
K_{CuL}' , M ⁻¹	5	125 (35)	188 (7)	2350 (120)
	15	134 (67)	170 (5)	1840 (50)
	25		160 (4)	1410 (50)
	35		145 (3)	1170 (30)
ΔH° , kcal mol ⁻¹	25		-1.43 (9)	-4.03 (14)
ΔS° , cal K ⁻¹ mol ⁻¹			5.3 (3)	0.92 (49)

intercept/slope ratio (see Figure 3).

For the Cu^{II} complexes formed with $[\text{12}] \text{aneS}_4$, $[\text{13}] \text{aneS}_4$, and $[\text{15}] \text{aneS}_5$, plots of the type described above were constructed for perchlorate ion concentrations of 0.010, 0.025, 0.050, 0.10, 0.25, 0.50, and 1.0 M at each of four temperatures: 5, 15, 25, and 35 °C. For the $\text{Cu}^{\text{II}}([\text{16}] \text{aneS}_4)$ system, the conditional stability constants were approximately 20-fold smaller, resulting in experimental data that were much more erratic. Therefore, data were obtained only for perchlorate concentrations of 0.010, 0.10, and 1.0 M. For all systems, the perchlorate ion concentrations were calculated to include the contribution from the $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ salt used (this contribution being significant for low perchlorate concentrations). The resolved K_{CuL}' values are listed in Tables I–IV.

For each Cu^{II} –ligand system, the temperature dependence of the K_{CuL}' value at constant perchlorate concentration can be used to calculate apparent enthalpy and entropy values according to the relationship

$$-\ln K_{\text{CuL}}' = \frac{\Delta H^{\circ'}}{RT} - \frac{\Delta S^{\circ'}}{R} \quad (11)$$

These values are included in Tables I–IV.

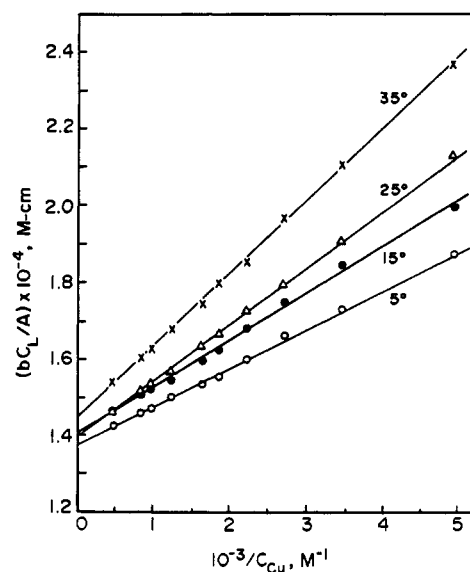


Figure 3. Spectrophotometric data for the $\text{Cu}^{\text{II}}([\text{15}] \text{aneS}_5)$ system plotted in the form of eq 10 to yield the apparent molar absorptivity value, ϵ_{CuL}' , as the reciprocal intercept and the conditional stability constant, K_{CuL}' , as the intercept/slope ratio. The data shown are for 0.010 M ClO_4^- ($\lambda = 414 \text{ nm}$).

Discussion

Reliability of Experimental Values. The molar absorptivity values listed in Tables I–IV are seen to vary considerably (but randomly) as the perchlorate concentration is varied. This variation is an artifact deriving, at least in part, from inaccuracies in the determination of the total polythia ether ligand concentration, C_L , as a result of experimental difficulties with the mercury(II) titrimetric method at the low ligand concentrations attainable. Therefore, these values are not quantitatively significant. They are included in the tables only for the purpose of providing a sense of their magnitude and to indicate the error within which the intercept was determined. Since, for a given perchlorate concentration, however, the same set of solutions were

Table IV. Conditional Stability Constants and Molar Absorptivity Values for the Cu^{II}([15]aneS₅) Complex in Aqueous Solution as a Function of Perchlorate Ion Concentration and Temperature ($\lambda = 414 \text{ nm}$)

param	T, °C	[ClO ₄], M						
		0.010	0.025	0.050	0.10	0.25	0.50	1.0
10 ⁻³ ε', M ⁻¹ cm ⁻¹	5	7.24 (2)	7.66 (1)	5.08 (3)	6.27 (3)	5.72 (2)	5.77 (3)	4.28 (6)
	15	7.08 (3)	7.57 (1)	5.01 (3)	6.21 (4)	5.70 (1)	5.63 (2)	4.26 (5)
	25	7.18 (1)	7.50 (1)	5.06 (3)	6.20 (2)	5.66 (1)	5.61 (2)	4.19 (4)
	35	6.89 (2)	7.37 (2)	4.89 (3)	6.08 (4)	5.56 (4)	5.44 (2)	4.11 (4)
10 ⁻³ K _{CuL'} , M ⁻¹	5	13.7 (2)	12.8 (3)	12.3 (12)	14.8 (16)	15.9 (16)	9.87 (130)	11.7 (32)
	15	11.7 (2)	10.9 (2)	10.6 (10)	13.6 (41)	12.8 (11)	8.38 (75)	8.98 (138)
	25	9.29 (2)	9.59 (12)	8.9 (66)	11.7 (9)	10.8 (5)	7.62 (67)	8.57 (111)
	35	7.82 (7)	8.03 (15)	7.9 (62)	10.2 (11)	9.68 (164)	8.44 (81)	8.25 (89)
ΔH ^o , kcal mol ⁻¹	25	-3.26 (19)	-2.60 (15)	-2.53 (2)	-2.19 (21)	-2.81 (23)	-0.93 (72)	-1.86 (62)
ΔS ^o , cal K ⁻¹ mol ⁻¹		7.26 (64)	9.45 (51)	9.62 (6)	11.3 (7)	9.08 (80)	14.8 (85)	11.8 (21)

Table V. Calculated Values for the Activity Coefficient Correction Term, $f_{\text{CuL}^+}/f_{\text{CuLX}^+}$, in Eq 23 as Calculated with and without the Empirical Linear $b\mu$ Term in Eq 24

T, °C	μ , M						
	0.010	0.025	0.050	0.10	0.25	0.50	1.00
Without $b\mu$ Term							
5	0.686	0.582	0.499	0.419	0.327	(0.269)	(0.226)
15	0.682	0.577	0.496	0.415	0.322	(0.266)	(0.221)
25	0.677	0.572	0.489	0.409	0.315	(0.260)	(0.215)
35	0.675	0.568	0.485	0.405	0.311	(0.256)	(0.211)
With $b\mu$ Term							
5	0.692	0.594	0.522	0.456	0.403	0.409	0.516
15	0.688	0.591	0.516	0.451	0.397	0.402	0.507
25	0.684	0.585	0.510	0.445	0.390	0.394	0.495
35	0.679	0.578	0.504	0.438	0.383	0.386	0.485

used for measurements at all four experimental temperatures, the decreasing trend in $\epsilon_{\text{CuL}'}$ with increasing temperature is a real phenomenon.

As noted in the preceding section, the values of $K_{\text{CuL}'}$ were calculated as the intercept/slope ratio from plots of eq 10. Although both the intercept and the slope are directly dependent on C_L , this term cancels out in taking the ratio of these two quantities. Hence, the $K_{\text{CuL}'}$ values are not dependent on the magnitude of the C_L values.

Treatment of the Conditional Stability Constants. The $K_{\text{CuL}'}$ values for Cu^{II}([12]aneS₄), Cu^{II}([13]aneS₄), and Cu^{II}([16]aneS₄), as listed in Tables I-III, exhibit a distinct increase as the perchlorate ion concentration is increased. This is consistent with the behavior previously observed for Cu^{II}([14]aneS₄).⁸ Therefore, a similar phenomenon would appear to be involved, the arguments for which will be recapped here only briefly.

The reaction involving only the aquated reactants and products (reaction 3) may be characterized by a simple concentration stability constant:

$$K_{\text{CuL}} = [\text{CuL}^{2+}] / [\text{Cu}^{2+}][\text{L}] \quad (12)$$

The relationship between K_{CuL} and the experimentally obtained conditional stability constant, $K_{\text{CuL}'}$, can be formulated in terms of α coefficients to correct for competing side reactions, viz.¹¹

$$K_{\text{CuL}'} = K_{\text{CuL}} \alpha_{\text{CuL}} / \alpha_{\text{Cu}} \alpha_{\text{L}} \quad (13)$$

where

$$\alpha_{\text{CuL}} = [\text{CuL}'] / [\text{CuL}^{2+}] \quad (14)$$

$$\alpha_{\text{Cu}} = [\text{Cu}'] / [\text{Cu}^{2+}] \quad (15)$$

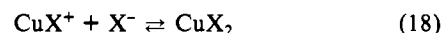
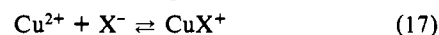
$$\alpha_{\text{L}} = [\text{L}'] / [\text{L}] \quad (16)$$

The polythia ether ligands do not protonate, and there are no other species available for complexation. Therefore, α_{L} is presumed to be unity and eq 13 simplifies to

$$K_{\text{CuL}'} = K_{\text{CuL}} \alpha_{\text{CuL}} / \alpha_{\text{Cu}} \quad (13a)$$

(11) The α coefficients are defined here as reciprocal fractional concentrations in accordance with Ringbom's convention: Ringbom, A. *Complexation in Analytical Chemistry*; Interscience: New York, 1963.

In the acidic medium used, perchlorate ion would appear to be the only species available to generate side reactions with either the aquocopper(II) ion or the Cu^{II}L complex. There are several reports in the literature¹²⁻¹⁴ of spectrophotometric and conductance data that indicate the existence of perchlorate (and tetrafluoroborate) adduct formation with solvated copper(II) ion in strongly polar coordinating solvents such as Me₂SO, acetonitrile, and water:



Thus, the expression for α_{Cu} may be represented as

$$\alpha_{\text{Cu}} = ([\text{Cu}^{2+}] + [\text{CuX}^+] + [\text{CuX}_2]) / [\text{Cu}^{2+}] \quad (19)$$

The experimental evidence indicates that, in general, the perchlorate ions are located in the outer-coordination sphere of the Cu(II) ion¹⁵ and are not tightly held by the metal ion so that α_{Cu} is not expected to be large in aqueous solution.

A similar expression for α_{CuL} may be formulated based on reactions 4 and 5, viz.

$$\alpha_{\text{CuL}} = ([\text{CuL}^{2+}] + [\text{CuLX}^+] + [\text{CuLX}_2]) / [\text{CuL}^{2+}] \quad (20)$$

There is little direct evidence for significant adduct formation between Cu(II) complexes and perchlorate ion in aqueous solution. In studying the redox properties of Cu(II)/Cu(I)-(Me₆[14]-dieneN₄), Endicott and co-workers¹⁶ reported indirect evidence for axial ligation by ClO₄⁻ from the apparent suppression of I⁻ coordination at the axial sites upon the addition of ClO₄⁻. On the basis of this observation, they suggested that ClO₄⁻ might be competing for the axial sites.

For the current systems involving Cu(II)-tetrathia ether complexes, we have observed that $K_{\text{CuL}'}$ increases with increasing perchlorate ion concentration. This implies that $\alpha_{\text{CuL}}/\alpha_{\text{Cu}} > 1$ in eq 13a, which forces us to conclude that perchlorate interacts with Cu^{II}L to a much greater extent than it does with Cu²⁺. In order to simplify the analysis of our data, we have attributed all of the changes in $K_{\text{CuL}'}$ to α_{CuL} by assuming that $\alpha_{\text{Cu}} \approx 1$, thereby further reducing eq 13a to the form

$$K_{\text{CuL}'} = K_{\text{CuL}} \alpha_{\text{CuL}} \quad (13b)$$

[Note: If the perchlorate ion does interact significantly with aquocopper(II) ion (i.e., if $\alpha_{\text{Cu}} \gg 1$), the perchlorate interactions with Cu^{II}L must occur to an even greater extent than indicated by the following analysis.]

Equation 20 may be rewritten as

$$\alpha_{\text{CuL}} = 1 + K_{1\text{X}}[\text{X}^-] + K_{1\text{X}}K_{2\text{X}}[\text{X}^-]^2 \quad (21)$$

(12) Johansson, L. *Coord. Chem. Rev.* **1974**, *12*, 241-261.

(13) (a) Libus, Z.; Sadowska, T. *J. Phys. Chem.* **1969**, *73*, 3229-3236. (b) Libus, W.; Chachulski, B.; Fraczyk, L. *J. Solution Chem.* **1980**, *9*, 355-369. (c) Libus, W.; Chachulski, B.; Grzybkowski, W.; Pilarczyk, M.; Puchalska, D. *Ibid.* **1981**, *10*, 631-648. (d) Grzybkowski, W.; Pilarczyk, M. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 2319-2331.

(14) Pethybridge, A. D. *Z. Phys. Chem. (Munich)* **1982**, *133*, 143-158.

(15) In some instances weak inner-sphere association between solvated Cu(II) ion and perchlorate ion is indicated: Diamond, A.; Fanelli, A.; Petrucci, S. *Inorg. Chem.* **1973**, *12*, 611-619.

(16) Palmer, J. M.; Papaconstantinou, E.; Endicott, J. F. *Inorg. Chem.* **1969**, *8*, 1516-1523. Me₆[14]dieneN₄ represents 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

where K_{1X} and K_{2X} are the equilibrium constants for reactions 4 and 5, respectively, expressed in terms of molar concentrations. Thus, on the basis of the premise that reactions 4 and 5 are the only side reactions of significance, eq 13b and 21 can be combined to yield

$$K_{CuL'} = K_{CuL} + K_{CuL}K_{1X}[X^-] + K_{CuL}K_{1X}K_{2X}[X^-]^2 \quad (22)$$

Since the experimental data indicate that the perchlorate interactions are weak, the last term in eq 22 should become insignificant when the perchlorate ion concentration is sufficiently small. Under these conditions, the data should conform to the limiting linear relationship

$$K_{CuL'} = K_{CuL} + K_{CuL}K_{1X}[X^-] \quad (22a)$$

[It is also perhaps worth noting that, in the lower perchlorate concentration range where eq 22a is valid, the value of α_{Cu} should more closely approximate unity.]

Activity Corrections. When the perchlorate ion concentration is varied over the range from 0.010 to 1.0 M, the ionic strength varies accordingly. Taking into account the activity corrections which must be applied to the K_{1X} term, eq 22a can be rewritten in the form

$$K_{CuL'} = K_{CuL}^\circ + K_{CuL}^\circ K_{1X}^\circ \left(\frac{f_{CuL}f_X}{f_{CuLX}} \right) [X^-] \quad (23)$$

where K_{CuL}° (obtained by extrapolation to infinite dilution) and K_{1X}° are activity stability constants, and f_{CuL} , f_X , and f_{CuLX} are the activity coefficients associated with CuL^{2+} , X^- , and $CuLX^+$, respectively.

For ionic strengths much above 0.10, the activity coefficient values are presumably best calculated by the empirically extended form of the Debye-Hückel equation¹⁷

$$\log f_i = \frac{-A(Z_i)^2\mu^{1/2}}{1 + Ba'\mu^{1/2}} + b\mu \quad (24)$$

where Z_i is the ionic charge, μ is the ionic strength, a' is the effective ionic diameter (in cm), and A and B are temperature-dependent cumulations of several physical constants including Avogadro's number (N_a), the electronic charge (e_0 , in esu), the bulk dielectric constant (D), the Boltzmann constant (k , in ergs K^{-1}), and the absolute temperature (T , K):

$$A = \left(\frac{2\pi N_a}{1000} \right)^{1/2} \frac{e_0^3}{2.303(DkT)^{3/2}} \quad (25)$$

$$B = \left(\frac{8\pi N_a}{1000} \right)^{1/2} \frac{e_0}{(DkT)^{1/2}} \quad (26)$$

The coefficient b in the empirical linear term of eq 24 has been evaluated as approximately 0.09 from experimental activity coefficient data for HCl in aqueous solution at 25 °C.¹⁸ This value has been presumed to be applicable for calculating the activity coefficients for X^- and $CuLX^+$ at all four temperatures studied. For the dipositive CuL^{2+} species, the value of b should be approximately four times (i.e., Z_i^2) larger, viz. 0.36.¹⁹

With the use of molecular models, a' values of 4×10^{-8} , 8×10^{-8} , and 10×10^{-8} cm have been estimated for X^- , CuL^{2+} , and $CuLX^+$, respectively. These effective ionic diameters are somewhat uncertain, particularly for CuL^{2+} and $CuLX^+$, which are not spherically symmetrical. Furthermore, the b coefficient in the linear term of eq 24 might be expected to reflect an ionic size dependency, but no precedence for such is to be found in the literature.

The resultant calculated values for the ratio $f_{CuL}f_X/f_{CuLX}$ are tabulated in Table V as computed both with and without the inclusion of the $b\mu$ term. At lower ionic strengths these ratio values

are essentially equal to f_{CuL} (since both X^- and $CuLX^+$ are univalent and their activity coefficients tend to cancel, especially in the region where $Ba'\mu^{1/2} \ll 1$) and should parallel the fourth power of the mean ionic activity coefficient as determined experimentally for univalent-univalent electrolytes. It is most reassuring, therefore, that the values of $f_{CuL}f_X/f_{CuLX}$, as calculated with the $b\mu$ term, are within 5% of the $(\gamma_{\pm})^4$ values determined experimentally for HBr (the largest univalent-univalent system for which extensive experimental data are available) up to an ionic strength of 0.50 M.²⁰

Resolution of K_{CuL}° and K_{1X}° . In view of the potential errors involved in the computation of the $f_{CuL}f_X/f_{CuLX}$ ratio at higher ionic strengths and the uncertainties as to the perchlorate concentrations at which the quadratic (i.e., K_{2X}) term in eq 22 may become appreciable, each set of $K_{CuL'}$ values for a specific ligand system at a single temperature was resolved according to eq 23 in five ways: (i) for $\mu \leq 0.10$ with the $f_{CuL}f_X/f_{CuL}$ ratios calculated without the $b\mu$ term; (ii) for $\mu \leq 0.25$ without $b\mu$; (iii) for $\mu \leq 0.25$ including $b\mu$; (iv) for $\mu \leq 0.50$ including $b\mu$; (v) for $\mu \leq 1.0$ including $b\mu$.

Among the first four approaches, the linear correlation coefficients and standard deviations were always worst when computed by method ii. The decreased linearity observed in the latter case is presumed to result from the inability of the Debye-Hückel equation to describe the activity coefficients adequately at $\mu = 0.25$ without the inclusion of the $b\mu$ term. By contrast, the resolved values and standard deviations for K_{CuL}° and K_{1X}° were generally closely comparable when methods i, iii, and iv were used. This provides strong support that the $b\mu$ terms are being reasonably estimated at ionic strengths of 0.25 and 0.50 M and that the quadratic term in eq 22 is negligible up to a perchlorate ion concentration of 0.50 M.

When method v is used, the $K_{CuL'}$ values for 1.0 M ClO_4^- were collinear with the values at lower ionic strengths for the [15]aneS₅ system, generally showed small to moderate positive deviations for the [12]aneS₄ and [13]aneS₄ systems, and exhibited large positive deviations for the [14]aneS₄ and [16]aneS₄ systems. These deviations suggest that, for the latter two systems, the formation of a diperchlorate adduct (reaction 5) becomes appreciable at high perchlorate concentration levels. However, the data were insufficient to permit a reliable estimation of the K_{2X} value. In these cases there is also some concern that the $CuLX_2$ species is contributing appreciably to the data at 0.50 M ionic strength. In the case of the [14]aneS₄ system, where sufficient data are available to examine this possibility,⁸ we find that the values of K_{CuL}° and K_{1X}° are nearly identical when resolved by either method i ($\mu \leq 0.10$) or method iv ($\mu \leq 0.50$). Thus, the K_{2X} (quadratic) term does not appear to be appreciable at 0.50 M ionic strength even for this system.

Since it seems preferable to utilize the widest possible range of perchlorate ion concentrations consistent with eq 23, the data for $\mu \leq 0.50$, as resolved by method iv, were included for the calculation of K_{CuL}° and K_{1X}° for each system at each temperature. The resulting resolved values are listed in Table VI. In the case of the [16]aneS₄ system, for which data were obtained only at ionic strengths of 0.010, 0.10, and 1.0 M, estimates of K_{CuL}° and K_{1X}° were obtained by using only the data for the two lower ionic strengths at 5 and 15 °C. Thus, no standard deviations are reported for this system.

The resolved values of K_{CuL}° and K_{1X}° , obtained by using method iv, were used to calculate the corresponding ΔH° and ΔS° values for each system by using the relationship in eq 11. These values are given in Table VII along with the corresponding calculated values of K_{CuL}° and K_{1X}° at 25 °C.

Characterization of the Perchlorate Interaction. Among the three systems for which K_{1X}° values were adequately resolved (i.e., the Cu(II) complexes with [12]-, [13]-, and [14]aneS₄), the 25 °C values are identical for all systems within the apparent ex-

(17) Reference 9; p 432.

(18) See Table IV in: Lin, C. T.; Rorabacher, D. B. *Inorg. Chem.* **1973**, *12*, 2402-2410.

(19) Davies, C. W. *J. Chem. Soc.* **1938**, 2093-2098.

(20) Reference 9, p 727, Table 12-2-1A. It should be noted that aquated H^+ has an effective ionic diameter of 9 Å, considerably larger than for any alkali metal ion.

Table VI. Resolved, Activity-Corrected K_{CuL}° and K_{1X}° Values for Cu^{II}([12]aneS₄), Cu^{II}([13]aneS₄), Cu^{II}([14]aneS₄), Cu^{II}([16]aneS₄), and Cu^{II}([15]aneS₅)

T, °C	Cu(II) complexes				
	[12]aneS ₄ ^a	[13]aneS ₄	[14]aneS ₄	[16]aneS ₄	[15]aneS ₅
			$10^{-3}K_{CuL}^\circ, M^{-1}$		
5	2.07 (±0.11)	1.65 (±0.18)	15.2 (±0.6)	0.114	14.10 (±1.18)
15	2.08 (±0.40)	1.59 (±0.07)	12.6 (±0.3)	0.128	12.20 (±0.98)
25	1.63 (±0.19)	1.44 (±0.09)	10.8 (±0.2)		10.18 (±0.83)
35	2.00 (±0.13)	1.27 (±0.07)	8.7 (±0.3)		8.47 (±0.63)
			K_{1X}°, M^{-1}		
5	18.1 (±1.1)	25.9 (±3.0)	30.6 (±1.4)	14.3	-0.93 (±0.88)
15	18.3 (±4.0)	20.8 (±1.1)	27.4 (±0.8)	7.4	-1.09 (±0.86)
25	23.6 (±3.0)	19.1 (±1.3)	24.2 (±0.5)		-0.81 (±0.88)
35	16.0 (±1.2)	18.7 (±1.2)	22.8 (±1.0)		0.38 (±0.82)

^aThe experimental data for 0.050 M ClO₄⁻ at 5, 15, and 35 °C were statistically eliminated from the data resolution for Cu^{II}([12]aneS₄).

Table VII. Thermodynamic Parameters for Activity-Corrected Copper(II) Complex Stability Constants and Perchlorate Adduct Formation Constants for Cu^{II}([12]aneS₄), Cu^{II}([13]aneS₄), Cu^{II}([14]aneS₄), Cu^{II}([16]aneS₄), and Cu^{II}([15]aneS₅)

param	Cu(II) complexes				
	[12]aneS ₄	[13]aneS ₄	[14]aneS ₄	[16]aneS ₄	[15]aneS ₅
$\Delta H_{CuL}^\circ, kcal\ mol^{-1}$	-0.62 (±1.02)	-1.49 (±0.28)	-3.13 (±0.15)		-2.91 (±0.18)
$\Delta S_{CuL}^\circ, cal\ K^{-1}\ mol^{-1}$	12.9 (±3.5)	9.4 (±1.0)	7.9 (±0.5)		8.6 (±0.6)
$10^{-3}K_{CuL}^\circ$ at 25 °C (calcd)	1.88	1.40	10.5	~0.09	10.3
$\Delta H_{1X}^\circ, kcal\ mol^{-1}$	-0.15 (±1.52)	-1.82 (±0.49)	-1.71 (±0.12)		<i>a</i>
$\Delta S_{1X}^\circ, cal\ K^{-1}\ mol^{-1}$	5.3 (±5.2)	-0.2 (±1.7)	0.6 (±0.4)		<i>a</i>
K_{1X}° at 25 °C (calcd)	18.7	19.5	24.2	~10	0

^aNo estimate.

perimental error, having a total relative range of about 20%. This indicates that a similar interaction is involved in each case. Although the resolved K_{1X}° values are less than 1 order of magnitude greater than the ion pair formation constant as calculated for CuL²⁺ interacting with ClO₄⁻, electrostatic attraction cannot account for the observed adduct formation since simple ion-pair formation would also be anticipated for Cu(H₂O)₆²⁺ with ClO₄⁻, and this latter interaction was specifically ignored in the resolution of K_{CuL}° and K_{1X}° according to eq 23 (i.e., α_{Cu} was assigned a value of 1). Thus, the magnitude of K_{1X}° represents the extent of CuLX⁺ formation over and above electrostatic contributions.

In the case of the [15]aneS₅ system, the data in Table VI reveal that, at all temperatures investigated, K_{1X}° is not statistically different from zero. Thus, there is no evidence for any perchlorate adduct formation with this system—even at perchlorate concentrations as high as 1.0 M. The crystal structure for the Cu^{II}([15]aneS₅) complex shows that it is a five-coordinate square-pyramidal species with the sulfur donor atoms occupying all five inner-sphere sites.²¹ All of the other Cu(II) complexes included in this study have one or two H₂O molecules or ClO₄⁻ ions axially coordinated in the crystalline state.²² This direct correlation between the availability of axial sites and the apparent formation of perchlorate adducts provides strong suggestive evidence that the perchlorate ion is occupying an inner-sphere site.

It is also interesting to note that the two systems which appear to exhibit evidence of adding a second perchlorate at high (1.0 M) perchlorate ion concentrations, viz. the [14]aneS₄ and [16]aneS₄ complexes, also were found to have two axially coordinated perchlorates in the crystalline state. This qualitative evidence would appear to corroborate the hypothesis that the perchlorate adducts involve axially coordinated perchlorate ions.

For the three systems for which ΔH_{1X}° and ΔS_{1X}° values have been obtained (i.e., the systems involving [12]-, [13]-, and [14]aneS₄), it is of interest to note that the ΔS_{1X}° values are not

statistically different from zero. Unfortunately, in the case of the [12]aneS₄ complex, the thermodynamic parameters are too imprecise to draw definitive conclusions. However, for the [13]aneS₄ and [14]aneS₄ systems, it is clear that the sole driving force for the perchlorate adduct formation is contained within the ΔH_{1X}° term. This does not necessarily reflect the heat of formation of a Cu-OCIO₃ bond relative to a displaced Cu-OH₂ bond since changes in hydrogen bonding to the surrounding outer solvation sphere may also be a significant factor. The fact that Cu^{II}([13]aneS₄) and Cu^{II}([14]aneS₄) have essentially identical parameters is particularly significant, however, since the former complex is square pyramidal while the latter is tetragonal.²²

Related Studies. In related but incomplete studies, we have observed qualitatively similar effects of perchlorate ion upon the conditional stability constants of the Cu(II)-tetrathia ether complexes involving open-chain (rather than cyclic) ligands. As noted in the Introduction, similar results are also obtained for solutions containing acids or salts of BF₄⁻ or CF₃SO₃⁻.

Surprisingly, the only anion investigated to date that does not appear to increase the value of the conditional stability constants is NO₃⁻. Whether this is due to a lack of interaction with the Cu(II)-tetrathia ether complexes or to an offsetting competition for the aquocopper(II) ion is unclear. Extensive studies on the influence of NO₃⁻ are rendered difficult by the observation that the addition of large amounts of NO₃⁻ results in the apparent oxidation of the polythia ether ligands, particularly in very acidic solutions.

Kinetic studies²³ on the formation and dissociation of the Cu(II)-tetrathia ether complexes reveal that, with increasing perchlorate ion, the formation rate constants increase slightly while the dissociation rate constants exhibit marked decreases of 10-fold or more. These results will be presented elsewhere in greater detail.

Significance. The current data analysis raises the serious question as to whether the formation of similar anion adducts is a general phenomenon in all Cu(II) complexes or is uniquely promoted by the coordination of the weakly bonding thia ether sulfur donor atoms. In systems involving other donor atoms, the formation of such anion adducts could easily go undetected in view of the accompanying effects of varying ionic strength upon ligand

(21) 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.

(22) 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.

(23) Diaddario, L. L.; Rorabacher, D. B., unpublished results.

protonation constants (which are nonexistent in the thia ether systems) and upon electrostatic interactions of the positively charged Cu(II) with charged ligands (also absent in the current systems). The apparent absence of significant adducts with $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ and $\text{Cu}([\text{15}] \text{aneS}_2)^{2+}$ in this study indicates that this phenomenon is not universal. However, future investigators might be well advised to check out the possibility of such adduct formation when equilibrium data are analyzed.

Conclusions

1. The conditional stability constants (K_{CuL}') for the Cu(II)-tetrathia ether complexes appear to increase by approximately 20-fold when the perchlorate ion concentration is increased from 0.01 to 1.0 M. This effect is independent of the cation, but qualitatively similar results are obtained in the presence of BF_4^- or CF_3SO_3^- .

2. The increase in the conditional stability constants is attributed to the formation of a perchlorate adduct, CuLX^+ , for which the formation constant, K_{1X}° , appears to exhibit a value of approximately 20 M^{-1} for each Cu(II)-tetrathia ether complex studied. The K_{1X}° values may be somewhat in error due to errors in activity coefficient calculations, the presence of significant side reactions with Cu^{2+} (which were ignored in our analysis), or contributions from the K_{2X} term in eq 22. Nonetheless, the

evidence suggests that interactions between the perchlorate ion and the Cu(II)-tetrathia ether complexes do exist and that the perchlorate is most probably associated within the inner-coordination sphere of the Cu(II) ion.

3. The corrected values for the Cu(II)-tetrathia ether complex stability constants (K_{CuL}°) extrapolated to zero perchlorate ion concentration are approximately 80% as large as the conditional stability constant values determined experimentally in the presence of 0.010 M ClO_4^- or 50–60% of the conditional values determined at 0.10 M ClO_4^- .

4. The evidence suggesting the coexistence of two forms of copper(II) complex in solution containing perchlorate ion (i.e., CuL^{2+} and CuLX^+) implies that the physical parameters measured for these systems, such as equilibrium constants and reaction rate constants, are composite values that cannot be directly interpreted. The resolution of meaningful constants, including thermodynamic functions and activation parameters, can only be achieved by studying these systems under conditions of varying perchlorate ion concentration.

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Kinetics and Mechanism of the Substitution of Dibenzoylmethanate for Acetylacetonate in $\text{UO}_2(\text{acac})_2\text{L}$ (L = Dimethyl Sulfoxide, *N,N*-Dimethylformamide, and Trimethyl Phosphate)

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Kinetics of the substitution of dibenzoylmethanate (dbm) for one acetylacetonate in $\text{UO}_2(\text{acac})_2\text{L}$ (acac = acetylacetonate; L = Me_2SO (dimethyl sulfoxide), dmf (*N,N*-dimethylformamide), and tmp (trimethyl phosphate)) have been studied in solvents L by spectrophotometry. Under the conditions $[\text{UO}_2(\text{acac})_2\text{L}] \gg [\text{Hdbm}]$, the rate law for the substitution reactions is expressed as rate = $k_2K[\text{UO}_2(\text{acac})_2\text{L}][\text{Hdbm}]/(1 + K[\text{UO}_2(\text{acac})_2\text{L}])$, where $K = [\text{UO}_2(\text{acac})_2\text{dbmH}]/[\text{UO}_2(\text{acac})_2\text{L}][\text{Hdbm}]$. The equilibrium constant K decreases as the basicity of ligand L increases. Rate constant k_2 corresponds to that of proton transfer from coordinated Hdbm to leaving acac in $\text{UO}_2(\text{acac})_2\text{dbmH}$, which is evidenced by the deuterium isotope effect on the rate and the linearity of the plot of $\log k_2$ vs. the reciprocal dielectric constant. The rate of the k_2 path is accelerated in amphiprotic solvents. Rate constants (s^{-1}) at 25 °C and activation parameters ΔH^\ddagger (kJ mol^{-1}) and ΔS^\ddagger ($\text{J K}^{-1} \text{mol}^{-1}$) for the k_2 path are 11.6×10^{-3} , 31.3 ± 1.0 , and -177 ± 4 for $\text{UO}_2(\text{acac})_2\text{dmf}$ and 2.31×10^{-3} , 50.2 ± 0.4 , and -127 ± 14 for $\text{UO}_2(\text{acac})_2\text{tmp}$. These results are discussed in connection with those of the acac-exchange reactions in $\text{UO}_2(\text{acac})_2\text{L}$ and $\text{Th}(\text{acac})_4$.

Kinetics of exchange reactions between metal chelate complexes of various β -diketonates (HB) and free ligands have been studied by the NMR line-broadening method,¹⁻⁹ isotopic labeling method with ^{14}C ,¹⁰⁻¹² and spectrophotometric method.¹³ Although rates

of the exchange reactions differ greatly with central metal ions, mechanisms so far proposed are classified into three types according to the rate-determining step: (1) breaking of one of the metal-oxygen bonds;¹¹ (2) formation of an intermediate containing a dangling unidentate ligand (B^-) and an incoming ligand (HB in the enol form);⁹⁻¹² (3) intramolecular proton transfer from coordinated HB to leaving B^- .³⁻⁷ In previous papers^{1,2} we reported the kinetic study of exchange reactions of acac in $\text{UO}_2(\text{acac})_2\text{L}$ (acac = acetylacetonate; L = dimethyl sulfoxide (Me_2SO), *N,N*-dimethylformamide (dmf)) in *o*-dichlorobenzene and proposed the mechanism of type 1.

In this paper we report the kinetic results of substitution reactions of dibenzoylmethanate (dbm) for one acac in $\text{UO}_2(\text{acac})_2\text{L}$

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