

remove it as a cream-colored AgI precipitate prior to reacting with FpBF_4 .

Conclusions

^1H NMR and infrared data have established that halide abstraction from FpI by AgBF_4 in CHCl_3 or CH_2Cl_2 initially yields Fp_2I^+ , which then reacts with additional AgBF_4 to yield FpBF_4 . The overall reaction consists of two parts; complete conversion of FpI into Fp_2I^+ occurs before any FpBF_4 is detected.

Although evidence is presented suggesting that BF_4^- is metal coordinated in the complex FpBF_4 , such may not be the case with other anions. Beck and Schlöter¹⁸ found that the coordinating ability of various anions and solvents decreased in the order acetone $>$ $\text{BF}_4^- >$ $\text{CH}_2\text{Cl}_2 >$ PF_6^- for the highly analogous complexes $\text{CpM}(\text{CO})_3^+$ ($\text{M} = \text{Mo}, \text{W}$).

The preparative method for FpBF_4 outlined in the Experimental Section has an important implication in synthesizing

olefinic complexes of the formula $\text{Fp}(\text{olefin})^+$. When the reaction mixture is cooled as described in the Experimental Section, samples of FpBF_4 free of Fp_2I^+ and $\text{Fp}(\text{H}_2\text{O})^+$ can be obtained. This would greatly simplify the purification of the desired olefin complex, especially in the case of less stable complexes.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support. We also thank Glen Bigam for obtaining the NMR spectra and for helpful discussions.

Note Added in Proof. It has come to our attention that the crystal structure of Fp_2IBF_4 , obtained from the reaction of FpI with AgBF_4 in dry benzene, has been reported: Cotton, F. A.; Frenz, B. A.; White, A. J. *J. Organomet. Chem.* 1973, 60, 147.

Registry No. FpBF_4 , 76391-69-0; $\text{Fp}_2\text{I}^+\text{BF}_4^-$, 12212-41-8; FpI , 12078-28-3; AgBF_4 , 14104-20-2; $\text{Fp}(\text{H}_2\text{O})^+$, 62077-07-0; $\text{FpI}(\text{Ag})^+$, 76391-70-3.

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Macrocyclic, Ring Size, and Anion Effects As Manifested in the Equilibrium Constants and Thermodynamic Parameters of Copper(II)–Cyclic Polythia Ether Complexes

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The equilibrium constants for $\text{Cu}(\text{II})$ reacting with two open-chain tetrathia ethers, five cyclic tetrathia ethers, and a cyclic pentathia ether (i.e., Me_2 - and Et_2 -2,3,2- S_4 ; 12-, 13-, 14-, 15-, and 16-ane- S_4 ; and 15-ane- S_5) have been determined spectrophotometrically in aqueous solution at 5, 15, 25, and 35 °C in a medium of 0.10 M HClO_4 . In this medium the 25 °C stability constants range from 94 M^{-1} for the Me_2 -2,3,2- S_4 complex to a maximum of $2.2 \times 10^4 \text{ M}^{-1}$ for the 14-ane- S_4 complex. As the ring size increases, the apparent ΔS° value exhibits a steady decrease from +15.9 eu for the complex formed with the smallest cyclic ligand, 12-ane- S_4 , to -5.4 eu for infinite ring size as represented by the open-chain ligand Me_2 -2,3,2- S_4 . The corresponding apparent ΔH° values progress from 0 kcal mol^{-1} for 12-ane- S_4 through a minimum value of -4.2 kcal mol^{-1} for 14-ane- S_4 to -1.4 kcal mol^{-1} for 16-ane- S_4 , decreasing once again for the open-chain ligand complexes. As the concentration of perchlorate ion is increased at constant temperature, the apparent stability constants also increase for all of these complexes. This phenomenon has been quantitatively investigated for the 14-ane- S_4 system and has been shown to fit a model in which perchlorate ion combines to form either a tight ion pair or a ternary complex which markedly enhances the apparent stability of the copper–polythia ether complex. The activity-corrected equilibrium constant and thermodynamic parameters for the perchlorate association with $\text{Cu}^{\text{II}}(14\text{-ane-S}_4)$ are as follows: $K(25 \text{ }^\circ\text{C})$, $24.1 \pm 0.5 \text{ M}^{-1}$; ΔH° , $-2.1 \pm 0.3 \text{ kcal mol}^{-1}$; ΔS° , $-0.7 \pm 1.1 \text{ eu}$.

Introduction

One of the unique properties observed for macrocyclic multidentate ligands is their ability to form more stable metal ion complexes than do their open-chain analogues. In studies on Cu^{II} -tetraamine complexes, Cabiness and Margerum² originally attributed this *macrocyclic effect* to a combination of the restricted configuration (an entropic effect) and the diminished solvation (primarily an enthalpic effect) of the *free* macrocyclic ligands relative to their open-chain analogues. Subsequently, Hinz and Margerum³ concluded that ligand solvation was by far the more important effect in the case of hydrogen-bonding ligands such as the tetraamines when operating in aqueous solution.

In expressing a contrasting point of view, Paoletti, Fabbrizzi, and Lever⁴ as well as Kodama and Kimura⁵ concluded that the macrocyclic effect manifested in the Cu^{II} -tetraamine complexes is dominated by an entropy effect. Although this

view was later modified,⁶ the relative importance of the enthalpic and entropic contributions to the macrocyclic effect was not clarified.

Recently, Clay, Paoletti, and co-workers⁷ have reported the results of direct measurements on the solvation enthalpies of the 14-membered cyclic tetraamine ligand (14-ane- N_4 or cyclam), which exhibits the maximum macrocyclic effect with $\text{Ni}(\text{II})$ and $\text{Cu}(\text{II})$, and an open-chain analogue (2,3,2- N_4 or 2,3,2-tet). As measured in 0.5 M NaOH (to prevent ligand protonation), the aqueous heats of solution for these two ligands are -2.5 and -15.8 kcal mol^{-1} , respectively.⁷ With the assumption that the metal complexes with these two ligands show little difference in solvation, these results appear to corroborate Hinz and Margerum's contention that free ligand solvation enthalpy is, indeed, the primary contributor to the macrocyclic effect *as manifested by the polyamine ligands in aqueous solution*.

As a result of the dominance of the ligand solvation term, other contributions to the macrocyclic effect cannot be quantitatively assessed from data gathered on the tetraamine

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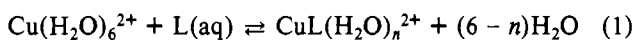
ligand systems. It is presumed, however, that such factors could be evaluated for complexes involving nonhydrogen-bonding ligands (or for solvents with low solvating power) where solvation effects could be minimized.

In earlier work⁸ we have demonstrated that the polythia ethers represent a homologous series of ligands which are not highly solvated in aqueous or alcoholic solutions. Accordingly, we have shown that the maximum macrocyclic effect manifested by the Cu^{II}-tetrathia ether complexes amounts to a 220-fold enhancement in the 25 °C stability constant value in 80% methanol.⁸ This is within experimental error of the 180-fold ratio determined both for these same complexes in aqueous solution⁹ and for the corresponding Ni^{II}-tetrathia ether complexes in nitromethane.¹⁰

The much smaller macrocyclic effect observed for the tetrathia ether complexes relative to the tetraamine complexes (where a 10⁶-fold enhancement is observed) is indicative of the huge contribution of ligand solvation enthalpy to the equilibrium phenomenon in amine systems. Moreover, the lack of dependence of the tetrathia ether macrocyclic effect on the nature of the solvent matrix (i.e., water, 80% methanol, and nitromethane) supports the hypothesis that ligand solvation effects are minimal for this series of ligands. However, to date no values have been generated for the overall entropy and enthalpy associated with polythia ether complex formation in solution.

We now wish to report the thermodynamic values associated with the formation of an entire series of Cu(II) complexes with open-chain and cyclic polythia ethers. These measurements have been conducted in aqueous solution to avoid potential interferences arising from changes in metal ion solvation as a function of temperature (as might be experienced in 80% methanol) and to provide data equivalent to the aqueous Cu^{II}-tetraamine studies.

The very low solubility of the polythia ether ligands in aqueous solution (<10⁻⁵ M) precludes the direct mixing of solvated reactants for the purpose of making calorimetric measurements or making direct measurements on the equilibrium concentrations representative of reaction 1. This



problem has been circumvented in this work by dissolving solid ligand samples in aqueous Cu(II) solutions. Although the resultant ligand concentrations were still very low, the strong visible absorption bands¹¹ attributable to S → Cu charge transfer¹² have made it possible to obtain precise spectrophotometric measurements on the dependence of complex formation on Cu(II) concentration at 5, 15, 25, and 35 °C.

The specific ligands studied include five cyclic tetrathia ethers, one cyclic pentathia ether, and two open-chain tetrathia ethers, viz., 1,4,7,10-tetrathiacyclododecane (12-ane-S₄), 1,4,7,10-tetrathiacyclotridecane (13-ane-S₄), 1,4,8,11-tetrathiacyclotetradecane (14-ane-S₄), 1,4,8,12-tetrathiacyclopentadecane (15-ane-S₄), 1,5,9,13-tetrathiacyclohexadecane (16-ane-S₄), 1,4,7,10,13-pentathiacyclopentadecane (15-ane-S₅), 2,5,9,12-tetrathiatridecane (Me₂-2,3,2-S₄), and 3,6,10,13-tetrathiapentadecane (Et₂-2,3,2-S₄). All eight ligands are illustrated in Figure 1.

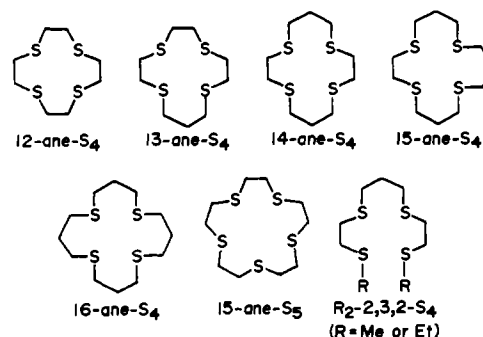
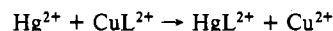


Figure 1. Ligands included in this work.

During the course of this work (and in related kinetic studies), a significant dependence of the stability constant (and the complex dissociation rate constant) on the concentration of perchlorate anion has been observed. This effect is not unique to perchlorate ion but exists with other noncomplexing anions (e.g., BF₄⁻ and CF₃SO₃⁻) as well. This phenomenon has been quantitatively examined in the case of the Cu^{II}(14-ane-S₄) complex. By varying the perchlorate ion concentration at each temperature, we resolved two components of the apparent stability constant and evaluated the individual thermodynamic parameters.

Experimental Section

Reagents. Preparation and purification of Cu(ClO₄)₂ and the several polythia ether ligands have been previously described.⁹ A stock Cu(II) solution was prepared by dissolving Cu(ClO₄)₂ in distilled, deionized water, diluting to volume, and standardizing by titration with EDTA. Stock Cu^{II}-polythia ether solutions were then prepared by adding a small weighed sample of the solid ligand to an aliquot of the Cu(II) solution, allowing the solution to stir overnight, removing any undissolved ligand by filtration through a fine glass frit, and diluting to volume. The total polythia ether concentration of each resultant solution was determined by potentiometric titration with standard Hg(II) solution according to the displacement reaction



using a Corning Model 12 pH meter equipped with a Reilly mercury-pool electrode (as the indicating electrode) and a Ag/AgCl reference electrode.

Spectrophotometric Measurements. For each series of spectrophotometric measurements, variable aliquots of the stock Cu(II) solution were added to constant aliquots of the appropriate Cu^{II}-polythia ether stock solution and diluted to volume after the addition of HClO₄ sufficient to adjust the total perchlorate ion concentration to the desired value. The same series of solutions were used for absorbance measurements at all four temperatures. Corrections for temperature-induced volume changes were initially made but proved to be insignificant within the precision of the spectrophotometric measurements and were ultimately ignored. All absorbance measurements were made with either a Beckman Acta V or a Cary 17D recording spectrophotometer, both instruments being equipped with thermostated cell holders. So that accurate temperature readings could be ensured, a calibrated thermistor was inserted directly into the spectrophotometric cell. Maximum sensitivity was obtained by selecting the S(σ) → Cu charge-transfer peak in the vicinity of 400 nm (ε ~ 6000–10000) for all absorbance measurements with the solutions contained in 5- or 10-cm cells.

Results

Stability Constant Measurements. At the wavelengths utilized, the free Cu(II) ion and the free ligand do not contribute significantly to the solution absorbance. Since the polythia ethers do not protonate and only 1:1 complexes are formed, the absorbance, *A*, may be related to the copper complex concentration, [CuL], by means of eq 2 where ε_{CuL}

$$A = \epsilon_{\text{CuL}} b [\text{CuL}] \quad (2)$$

is the molar absorptivity of the CuL complex at the wavelength

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Table I. Resolved Stability Constants and Molar Absorptivity Values for Copper(II)-Polythia Ether Complexes in Aqueous Solution as a Function of Temperature in 0.10 M HClO₄

parameters	12-ane-S ₂	13-ane-S ₄	14-ane-S ₄	15-ane-S ₄	16-ane-S ₄	15-ane-S ₅	Me ₂ -2,3,2-S ₄	Et ₂ -2,3,2-S ₄	
λ_{\max} , nm	387	390	390	414	440	414	407	410	
$10^{-3}\epsilon_{\text{CuL}}$, M ⁻¹ cm ⁻¹	5 °C	6.14 (1)	6.63 (1)	8.32 (1)	10.9 (1)	9.35 (3)	6.18 (1)	8.07 (1)	7.51 (1)
	15 °C	6.04 (1)	6.56 (1)	8.20 (1)	10.6 (1)	8.87 (3)	6.12 (1)	7.89 (1)	7.18 (2)
	25 °C	5.93 (2)	6.46 (1)	8.04 (3)	10.4 (1)	8.24 (2)	6.05 (1)	7.87 (2)	6.84 (1)
	35 °C	5.85 (1)	6.36 (1)	7.93 (2)	10.0 (1)	7.93 (2)	5.99 (1)	8.12 (3)	6.32 (1)
$10^{-3}K_{\text{CuL}}$, M ⁻¹	5 °C	2.41 (2)	3.77 (6)	34.9 (4)	2.23 (3)	0.188 (3)	22.2 (8)	0.151 (1)	0.243 (4)
	15 °C	2.46 (3)	3.07 (2)	27.5 (2)	1.94 (2)	0.170 (2)	18.5 (5)	0.122 (1)	0.196 (2)
	25 °C	2.47 (3)	2.77 (2)	21.8 (3)	1.49 (2)	0.160 (1)	15.3 (2)	0.094 (1)	0.151 (2)
	35 °C	2.45 (3)	2.46 (2)	16.5 (1)	1.28 (1)	0.145 (1)	13.1 (3)	0.071 (1)	0.128 (1)

used and b is the path length (in cm) of the spectrophotometric cell.

Due to the small stability constants involved and the limited solubility of the ligands, reaction 1 could not generally be forced completely to the right. Thus, the value of $[\text{CuL}]$ was unknown, making it impossible to calculate ϵ_{CuL} directly from a single solution measurement. So that this difficulty could be circumvented, the method of McConnell and Davidson¹³ was employed in which both ϵ_{CuL} and the stability constant, K_{CuL} (eq 3), were treated as unknowns. With definition of

$$K_{\text{CuL}} = [\text{CuL}]/([\text{Cu}][\text{L}]) \quad (3)$$

the analytical concentrations of Cu(II) and ligand as C_{Cu} and C_{L} , respectively (eq 4 and 5), and with conditions where, in

$$C_{\text{Cu}} = [\text{Cu}] + [\text{CuL}] \quad (4)$$

$$C_{\text{L}} = [\text{L}] + [\text{CuL}] \quad (5)$$

all solutions, $C_{\text{Cu}} \gg C_{\text{L}}$, it follows that $[\text{Cu}] \approx C_{\text{Cu}}$ such that eq 3-5 can be combined to yield eq 6. Substitution of eq

$$[\text{CuL}] = K_{\text{CuL}}C_{\text{Cu}}C_{\text{L}}/(K_{\text{CuL}}C_{\text{Cu}} + 1) \quad (6)$$

6 into eq 2 and rearrangement yield the linear relationship¹³ of eq 7. So that we may account for any side reactions which

$$\frac{bC_{\text{L}}}{A} = \frac{1}{\epsilon_{\text{CuL}}} + \frac{1}{\epsilon_{\text{CuL}}K_{\text{CuL}}C_{\text{Cu}}} \quad (7)$$

occur, the stability constants obtained spectrophotometrically may be regarded as conditional constants, K_{CuL}' , as defined by eq 8, where the primed concentration terms $[\text{CuL}']$, $[\text{Cu}']$,

$$K_{\text{CuL}}' = [\text{CuL}']/([\text{Cu}'][\text{L}']) \quad (8)$$

and $[\text{L}']$ represent all forms of the copper complex, the uncomplexed copper, and the uncomplexed ligand, respectively. Thus, under specified solution conditions, eq 7 should be treated in the modified format of eq 9 where ϵ_{CuL}' is the apparent molar absorptivity of CuL' .

$$\frac{bC_{\text{L}}}{A} = \frac{1}{\epsilon_{\text{CuL}}'} + \frac{1}{\epsilon_{\text{CuL}}'K_{\text{CuL}}'C_{\text{Cu}}} \quad (9)$$

Plotting bC_{L}/A against $1/C_{\text{Cu}}$ yields ϵ_{CuL}' as the reciprocal intercept and K_{CuL}' as the intercept/slope ratio. Since the value calculated for K_{CuL}' depends on both the intercept and the slope, it is necessary to operate under concentration conditions where both parameters can be accurately evaluated (at very high reactant concentrations the slope is poorly defined while at low concentrations the intercept is inaccurate). For each system, the copper concentration range required to achieve these conditions is inversely related to the magnitude of the conditional stability constant. Figure 2 illustrates a typical set of plots for the $\text{Cu}(\text{Et}_2\text{-2,3,2-S}_4)^{2+}$ complex, a system exhibiting one of the highest temperature dependencies among the polythia ether systems studied.

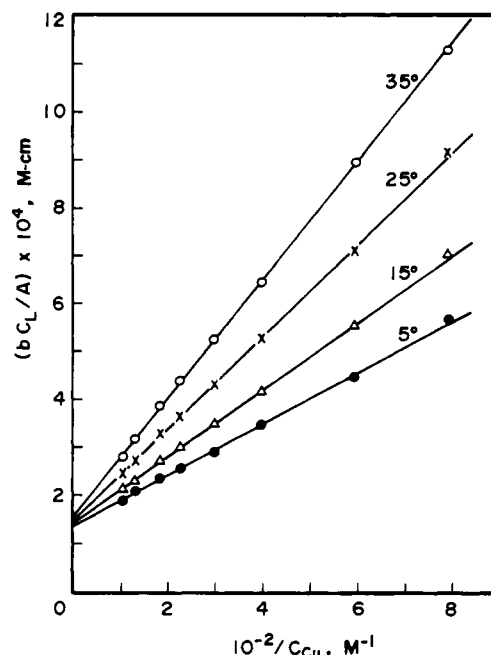


Figure 2. Typical spectrophotometric data plotted in the form of eq 9 to yield the apparent molar absorptivity of the Cu(II) complex as the reciprocal intercept and the conditional stability constant as the intercept/slope ratio. Data shown are for the complex formed with the open-chain tetrathia ether ligand $\text{Et}_2\text{-2,3,2-S}_4$.

The actual wavelengths used and the resolved values of ϵ_{CuL}' and K_{CuL}' for each of the four experimental temperatures are listed in Table I for all eight Cu^{II}-polythia ether complexes. All values were determined from linear least-squares calculations which yielded the standard deviations given in parentheses following the entry.

The values of the formal thermodynamic parameters were determined by plotting eq 10 (where R is the gas constant in cal mol⁻¹ K⁻¹). Linear plots were obtained in all cases, yielding the data listed in Table II.

$$\frac{\Delta G^{\circ'}}{T} = -R \ln K_{\text{CuL}}' = \frac{\Delta H^{\circ'}}{T} - \Delta S^{\circ'} \quad (10)$$

Perchlorate Concentration Dependence. In testing the effect of varying reagent concentrations on the conditional equilibrium constants, we observed that K_{CuL}' increases with increasing HClO₄ concentration. By substitution of NaClO₄ and Cu(ClO₄)₂ for all or part of the HClO₄ normally added, this apparent increase in the stability of the CuL complex was shown to be independent of pH, ionic strength, and the nature of the cation but was directly related to the perchlorate ion concentration. This has been corroborated in kinetic studies where other noncomplexing anions (BF₄⁻ and CF₃SO₃⁻) have been shown to produce similar effects.¹⁴

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Table II. Apparent Thermodynamic Parameters for Copper(II)-Polythia Ether Complexes in Aqueous Solution (0.10 M HClO₄)

complexed ligand	ΔG° (25 °C), kcal mol ⁻¹	ΔH° (25 °C), kcal mol ⁻¹	ΔS° , eu	$d(\text{Cu-S})$, Å	$\nu(\text{Cu-S})$, cm ⁻¹ ^a
12-ane-S ₄	-4.63	+0.11 (5)	15.9 (2)	2.30-2.37	280
13-ane-S ₄	-4.69	-2.37 (23)	7.8 (8)	2.32 ^b	272
14-ane-S ₄	-5.92	-4.22 (21)	5.6 (7)	2.30 ^b	274
15-ane-S ₄	-4.33	-3.28 (31)	3.6 (11)	2.32 ^b	258
16-ane-S ₄	-3.00	-1.43 (9)	5.3 (3)	2.33, ^c 2.39 ^c	247
15-ane-S ₅	-5.70	-3.02 (6)	9.0 (2)	2.31, ^b 2.40 ^d	282
Me ₂ -2,3,2-S ₄	-2.69	-4.29 (28)	-5.4 (10)		
Et ₂ -2,3,2-S ₄	-2.97	-3.72 (18)	-2.5 (6)	2.33 ^b	276

^a Data from ref 12. ^b Four bond distances. ^c Two bond distances. ^d One Cu-S bond.

Table III. Conditional Stability Constants and Molar Absorptivity Values for the Cu^{II}(14-ane-S₄) Complex in Aqueous Solution as a Function of Perchlorate Ion Concentration and Temperature ($\lambda = 390$ nm)

parameter	[ClO ₄ ⁻], M						
	0.010	0.025	0.050	0.100	0.250 ^a	0.500	1.000 ^a
$10^{-3}\epsilon_{\text{CuL}}$, M ⁻¹ cm ⁻¹	5 °C	8.08 (10)	8.52 (5)	8.43 (2)	8.32 (1)		8.49 (2)
	15 °C	7.90 (11)	8.40 (4)	8.39 (2)	8.20 (1)		8.41 (1)
	25 °C	7.74 (11)	8.23 (6)	8.20 (1)	8.04 (3)	7.96 (2)	8.21 (1)
	35 °C	7.66 (15)	8.05 (7)	8.05 (1)	7.93 (2)		8.04 (1)
$10^{-3}K_{\text{CuL}}$, M ⁻¹	5 °C	18.4 (9)	23.3 (8)	27.4 (3)	34.9 (4)		110.5 (24)
	15 °C	15.5 (8)	18.1 (4)	21.2 (2)	27.5 (2)		82.2 (11)
	25 °C	12.7 (5)	14.9 (3)	17.42 (6)	21.8 (3)	36.2 (7)	62.2 (5)
	35 °C	10.2 (5)	12.0 (3)	13.69 (3)	16.5 (1)		46.91 (3)
ΔH° , kcal mol ⁻¹	25 °C	-3.34 (21)	-3.73 (9)	-3.86 (12)	-4.19 (21)		-4.85 (7)
ΔS° , eu		7.6 (7)	6.6 (3)	6.4 (4)	5.7 (7)		5.6 (2)

^a Data from ref 14.

So that a quantitative evaluation of this anion effect could be obtained, the Cu(14-ane-S₄) system was selected for further study since the higher stability of this complex permitted the use of lower reactant concentrations and, therefore, a wider range of perchlorate ion concentrations.

The apparent molar absorptivity and conditional stability constant values obtained for the Cu^{II}(14-ane-S₄) complex in five different perchlorate concentrations at each of four temperatures are listed in Table III. The formal enthalpy and entropy values applicable for each perchlorate concentration are also tabulated.

Discussion

Perchlorate Ion Dependence. It is presumed that the conditional stability constant, K_{CuL} , can be related to the thermodynamic stability constant, K_{CuL} , by means of α coefficients to correct for competing side reactions, viz.¹⁵

$$K_{\text{CuL}}' = K_{\text{CuL}}\alpha_{\text{CuL}}/\alpha_{\text{Cu}}\alpha_{\text{L}} \quad (11)$$

where

$$\alpha_{\text{CuL}} = [\text{CuL}']/[\text{CuL}] \quad (12a)$$

$$\alpha_{\text{Cu}} = [\text{Cu}']/[\text{Cu}] \quad (12b)$$

$$\alpha_{\text{L}} = [\text{L}']/[\text{L}] \quad (12c)$$

In order to formulate a reasonable interpretation of the stability constant data, therefore, it is necessary to identify the side reactions involved and to establish their contributions to the α coefficients.

In the case of the polythia ether ligands, there are no protonated species nor do these ligands react with any of the other cations present. Therefore, α_{L} is presumed to be unity.

In the acidic media used in this study, perchlorate is the only nucleophilic species present which could compete with the polythia ethers for the aquocopper ion. Although there is a

report of very weak perchlorate complexation with Cu(II),¹⁶ we have not been able to detect this species in our work. Moreover, the fact that $K_{\text{CuL}}'/\alpha_{\text{Cu}} > 1$ (eq 11) which requires that perchlorate interacts with the CuL complex to a much greater extent than it does with the aquated Cu(II) ion. Thus, for the purposes of our analysis, we have assumed that α_{Cu} is unity and have focused on the interaction of ClO₄⁻ with CuL.

The foregoing considerations lead us to propose that perchlorate ion (symbolized below as X⁻) forms one or more addition complexes with CuL as represented by eq 13 and 14,



where CuLX⁺ and CuLX₂ may be either inner- or outer-sphere complexes. Inclusion of these species in eq 12a yields eq 15.

$$\alpha_{\text{CuL}} = \frac{[\text{CuL}] + [\text{CuLX}] + [\text{CuLX}_2]}{[\text{CuL}]} \quad (15)$$

Defining the equilibrium constants for eq 13 and 14 as K_{1X} and K_{2X} , respectively, and substituting into eq 15 yields eq 16.

$$\alpha_{\text{CuL}} = 1 + K_{1X}[\text{X}] + K_{1X}K_{2X}[\text{X}]^2 \quad (16)$$

Assuming that both α_{Cu} and α_{L} are unity under the experimental conditions used and substituting eq 16 into eq 11 result in the quadratic relationship shown in eq 17. At sufficiently

$$K_{\text{CuL}}' = K_{\text{CuL}}(1 + K_{1X}[\text{X}] + K_{1X}K_{2X}[\text{X}]^2) \quad (17)$$

low perchlorate ion concentrations the last term in eq 17 should become insignificant, leaving the simplified linear relationship given in eq 18.

$$K_{\text{CuL}}' = K_{\text{CuL}} + K_{\text{CuL}}K_{1X}[\text{X}] \quad (18)$$

Since no inert anions have been identified which can be used with this system, it was impossible to vary [X] without si-

(15) (a) Schwarzenbach, G. "Complexometric Titrations"; Interscience: New York, 1957. (b) Ringbom, A. "Complexation in Analytical Chemistry"; Interscience: New York, 1963.

(16) Libus, Z.; Sadowska, T. *J. Phys. Chem.* **1969**, *73*, 3229.

Table IV. Calculated Values for the Activity Coefficient Correction Term,^a $f_{\text{CuL}^{\text{X}}}/f_{\text{CuLX}}$, in Eq 19

T, °C	μ , M						
	0.01	0.025	0.05	0.10	0.25	0.50	1.00
5	0.686	0.582	0.499	0.419		0.269	
15	0.682	0.577	0.496	0.415		0.266	
25	0.677	0.572	0.489	0.409	0.315	0.260	0.215
35	0.675	0.568	0.485	0.405		0.256	

^a Activity coefficient calculations based on the following assumed ionic diameters: X, 4 Å; CuL, 8 Å; CuLX, 10 Å.

multaneously varying the ionic strength. Thus, activity corrections must be applied to the last term in eq 18 in order to resolve the values of the two contributing stability constants

$$K_{\text{CuL}'} = K_{\text{CuL}}^{\circ} + K_{\text{CuL}}^{\circ} K_{1\text{X}}^{\circ} \left(\frac{f_{\text{CuL}^{\text{X}}}}{f_{\text{CuLX}}} \right) [\text{X}] \quad (19)$$

where K_{CuL}° (obtained by extrapolation to infinite dilution) and $K_{1\text{X}}^{\circ}$ represent activity constants. The activity coefficients are calculated by using the extended Debye-Hückel equation

$$\log f_i = \frac{-Az_i^2 \mu^{1/2}}{1 + Ba' \mu^{1/2}} \quad (20)$$

$$A = \left(\frac{2\pi N_a}{1000} \right)^{1/2} \frac{e_0^3}{2.303(DkT)^{3/2}} \quad (21)$$

$$B = \left(\frac{8\pi N_a}{1000} \right)^{1/2} \frac{e_0}{(DkT)^{1/2}} \quad (22)$$

where z_i is the ionic charge, μ is the ionic strength, a' is the ionic diameter (in cm), N_a is Avogadro's number, e_0 is the electronic charge (in esu), D is the dielectric constant of the medium, k is the Boltzmann constant (in ergs), and T is the absolute temperature. With the use of molecular models, values of 4, 8, and 10 Å were selected for the approximate ionic diameters of X⁻, CuL²⁺, and CuLX⁺, respectively.

The resulting calculated values of the activity coefficient correction term, $f_{\text{CuL}^{\text{X}}}/f_{\text{CuLX}}$, in eq 19 are listed in Table IV. With these values, eq 19 was plotted as shown in Figure 3.

At all temperatures, the value of $K_{\text{CuL}'}$ for 0.50 M ClO₄⁻ lies above the line established by the data obtained for 0.01–0.10 M ClO₄⁻ when plotted in the form of eq 19. At this higher ionic strength, eq 20 must be modified to eq 20a where

$$\log f_i = \frac{-Az_i^2 \mu^{1/2}}{1 + Ba' \mu^{1/2}} + b\mu \quad (20a)$$

b is an empirical constant. On the basis of experimental activity coefficient data for HCl, a value of b equal to approximately 0.09 has been obtained in aqueous solution at 25 °C.¹⁷ This value should be roughly applicable for calculating the activity coefficients for the univalent ions X⁻ and CuLX⁺. For the dipositive species, CuL²⁺, the value of b should be approximately 4 times (i.e., z_i^2) larger, viz., 0.36.¹⁸

With the utilization of activity coefficients calculated from eq 20a for all points, the plots of eq 19 are linear over the entire range of 0.01–0.50 M ClO₄⁻ with intercepts and slopes which are within 6% of those shown in Figure 3. However, within the range of 0.01–0.10 M ClO₄⁻, the linearity of the data points becomes slightly worse upon including the $b\mu$ correction term. In view of this and the inherent uncertainty of the appropriate b values to utilize, the values of K_{CuL}° and $K_{1\text{X}}^{\circ}$ obtained by linear-regression analysis using only the 0.01–0.10 M ClO₄⁻ data, without the inclusion of the empirical $b\mu$ term (as in

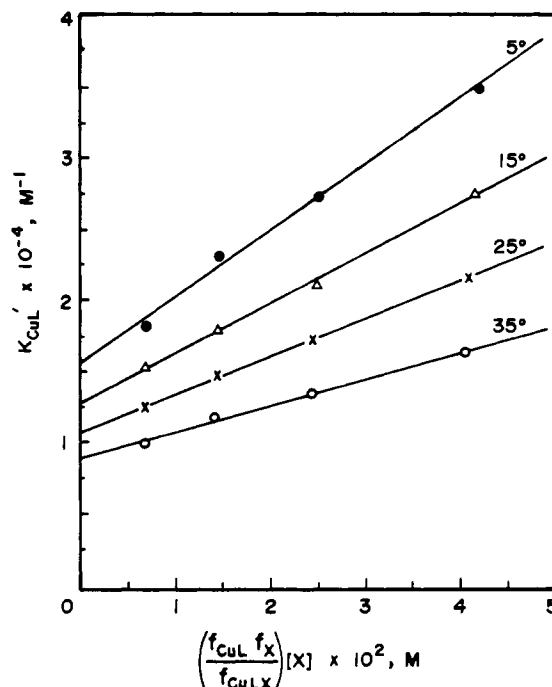


Figure 3. Resolution of the perchlorate dependence of the apparent stability constant, $K_{\text{CuL}'}$, for the Cu^{II}(14-ane-S₄) complex. The data are plotted in the form of eq 19 to yield the perchlorate-independent activity constant, K_{CuL}° , as the intercept and the perchlorate-dependent activity constant, $K_{1\text{X}}^{\circ}$, as the slope/intercept ratio for each temperature plotted.

Table V. Resolved, Activity-Corrected, Stability Constants and Corresponding Thermodynamic Parameters for the Binary Cu^{II}(14-ane-S₄) Complex and the Ternary Cu^{II}(14-ane-S₄) Perchlorate Complex in Aqueous Solution

T, °C	10 ⁻³ K _{CuL} [°] , M ⁻¹	K _{1X} [°] , M ⁻¹
5	15.9 (7)	29.0 (21)
15	13.1 (3)	26.4 (11)
25	11.0 (1)	24.1 (5)
35	9.2 (2)	19.9 (11)
ΔH_{25}° , kcal mol ⁻¹	-3.10 (5)	-2.07 (33)
ΔS° , eu	8.1 (2)	-0.7 (11)

Figure 3), are preferred. These values are listed in Table V along with the corresponding values for ΔH° as determined by plotting eq 10.

Although the experimental data points for 0.50 M ClO₄⁻ were not used in resolving the values listed in Table V, the fact that these points are collinear with the lower ionic strength data (when incorporating the empirical $b\mu$ correction term in eq 20a) indicates that only one perchlorate ion is interacting with the CuL complex over the entire range of 0.01–0.50 M ClO₄⁻. While the nature of this interaction is unclear, the experimental data suggest that this interaction involves more than electrostatic attraction. This conclusion is based primarily on the fact that simple ion pairing should be equally feasible with the aquocopper ion which would lead to an expression for α_{Cu} identical in format with that of eq 17. Since α_{Cu} has been assumed to be unity in our evaluation of $K_{1\text{X}}^{\circ}$, it is obvious from a comparison of eq 11 and 17 that the inclusion of ion-pairing considerations for Cu(H₂O)₆²⁺ with ClO₄⁻ would lead to even larger values of $K_{1\text{X}}^{\circ}$ for the CuLX⁺ species. In other words, simple ion pairing with ClO₄⁻ should be roughly equivalent for CuL(H₂O)₂²⁺ and Cu(H₂O)₆²⁺, leading to roughly equal values of α_{Cu} and α_{CuL} . In our treatment, this should have resulted in a $K_{1\text{X}}^{\circ}$ value of approximately 0 if simple electrostatic interactions represented the only significant forces between the CuL complex and ClO₄⁻.

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

(18) Davies, C. W. *J. Chem. Soc.* 1938, 2093.

In attempting to elucidate the nature of the interaction between the CuL complex and ClO_4^- , we have examined the visible absorption and resonance Raman spectra as a function of the perchlorate concentration. Both spectra show no significant changes until the perchlorate concentration is well above 1 M. The data in Table III also show that within experimental error the apparent molar absorptivity of CuL' at 390 nm does not change as the perchlorate ion concentration varies from 0.01 to 0.50 M. Since this peak has been identified as arising from $\text{S}(\sigma) \rightarrow \text{Cu}$ charge transfer, these observations indicate that the Cu-S bond distances and angles are not altered by the perchlorate interaction. However, the spectra provide no solid evidence as to whether inner-sphere or outer-sphere interactions are involved.

In the absence of direct evidence to the contrary, we presume that this CuL- ClO_4^- association may best be described as a tight ion pair. The greater proclivity for forming such a tight ion pair with the CuL species relative to the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ species may result from the fact that outer-sphere solvation is much weaker in the case of the former species relative to the latter. The increase in the conditional stability constant of CuL upon association with the ClO_4^- ion, however, presumably reflects changes in the outer-sphere solvation as influenced by the anion.

Macrocyclic and Ring Size Effects. In view of the effect of perchlorate ion concentration upon the apparent stability constants of the Cu^{II} -polythia ether complexes, the data obtained for the various complexes at 0.10 M HClO_4 can be wholly ascribed to the variations in the ring size of the ligands only if the contributions of the perchlorate ion to $K_{\text{CuL}'}$ are identical in all cases. In independent work we have noted that the aqueous kinetic behavior of the 12-, 13-, and 14-ane- S_4 complexes as a function of perchlorate ion concentration is very similar.¹⁴ Since these represent the most divergent complexes from a structural standpoint,¹⁹ it is presumed that all of the Cu^{II} -polythia ether complexes studied are, indeed, equally affected by the perchlorate ion. Therefore, we presume that the relative $K_{\text{CuL}'}$, ΔH° , and ΔS° values obtained at 0.10 M HClO_4 may be compared and interpreted in terms of the contributions of the macrocyclic and ring size effects.

For all Cu^{II} -polythia ether complexes, the resolved ΔH° and ΔS° values must include the contributions arising from the desolvation of $\text{Cu}(\text{H}_2\text{O})_6^{2+}$. From crystal structure data obtained in this laboratory,¹⁹ this amounts to a loss of four inner-sphere water molecules in the case of the tetragonal complexes formed by Cu(II) with 14-, 15-, and 16-ane- S_4 and Me_2 - and Et_2 -2,3,2- S_4 , five waters in the case of the square-pyramidal complexes formed with 12- and 13-ane- S_4 , and six waters in the case of square-pyramidal Cu^{II} (15-ane- S_5) (i.e., $n = 2, 1$, and 0 , respectively, in reaction 1). For the first five complexes, the two remaining apical Cu-H $_2$ O bonds are elongated as a result of the tetragonal distortion, whereas, for the small ring systems (12-ane- S_4 and 13-ane- S_4), the lone remaining apical Cu-H $_2$ O bond is foreshortened.

These considerations suggest that the enthalpic and entropic contributions of Cu(II) desolvation may be relatively consistent for the formation of the five tetragonal systems but may vary to some extent for the three square-pyramidal complexes. This

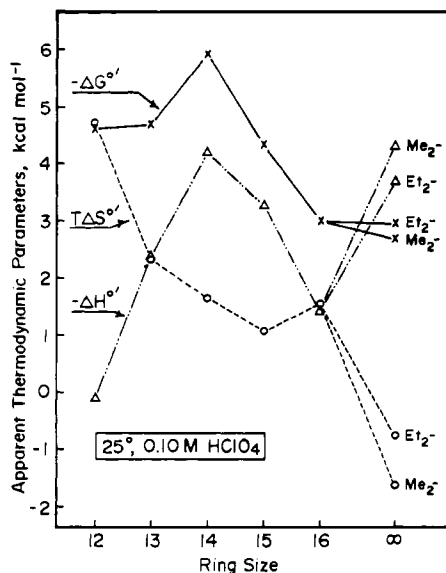


Figure 4. Ring size effects for the tetrathia ether complexes of Cu(II) as manifested in the apparent thermodynamic parameters for complex formation in aqueous solution at 25 °C and 0.10 M HClO_4 . The open-chain tetrathia ethers with terminal methyl (Me_2) and ethyl (Et_2) groups are represented as being of infinite ring size.

contribution to the thermodynamic trends appears to have been ignored by previous workers. To the extent that these factors are significant, the difference in metal desolvation should lead to more positive ΔS° and ΔH° values for the square-pyramidal species.

For purposes of visualization, the values of ΔG° , ΔH° , and $T\Delta S^\circ$ (25 °C) for the Cu^{II} -tetrathia ether complexes are plotted against ring size in Figure 4 to illustrate the trends in the relative thermodynamic constants. To the extent that perchlorate effects are constant for each ligand system, the reaction entropy is seen to decrease with increasing ring size with a slight perturbation for the 16-ane- S_4 complex.

Since, to a first approximation, it is presumed that all of the tetrathia ethers are comparable in rigidity when complexed to Cu(II), the observed trend in reaction entropies is presumed to reflect the greater loss of freedom of the flexible open chain and larger cyclic ligands upon complexation as suggested by earlier investigators. The positive entropy values associated with all of the cyclic ligands apparently arise from the fact that the entropy gain associated with metal ion desolvation more than offsets the entropy loss associated with ligand complexation. In this regard it is interesting to note that the entropy values obtained for the formation of the Cu^{II} -tetrathia ether complexes are, in all cases, about 20 eu smaller than the values previously reported for the corresponding Cu^{II} -tetraamine complexes.^{5,6} Since the metal ion and ligand ring sizes are essentially constant, this difference is consistent with the conclusion that ligand desolvation contributes extensively to the overall reaction entropies in the polyamine complexes.

The trend in ΔH° values roughly parallels the Cu-S bonding as revealed in structural data^{14,19} and is seen to account primarily for the ring size effects upon the stability constant values. Thus, among the cyclic tetrathia ether complexes, ΔH° is at a minimum in the Cu(14-ane- S_4) complex, reflecting the fact that Cu(II) fits most perfectly into the cavity of the 14-membered ligand. Although the cavity of the 15-ane- S_4 ligand is slightly too large, this ligand manages to flex sufficiently to maintain nearly identical Cu-S bonding without inducing undue strain into the ligand backbone. For 16-ane- S_4 , it appears that the ligand can no longer flex sufficiently to form optimal Cu-S bonds. Thus, two Cu-S bonds are slightly elongated in this complex,¹⁹ and an increase in ΔH° results.

(19) Crystallographic structural determinations indicate that the four sulfur donor atoms lie in a single plane for each of the cyclic tetrathia ether complexes of Cu(II) included in this work.

(20) Whereas the Cu(II) is coplanar with the four sulfurs in the complexes with the larger macrocycles (14-, 15-, 16-ane- S_4) with two water molecules axially coordinated in solution, the metal ion is approximately 0.3 Å above this plane in the 13-ane- S_4 complex and 0.5 Å above in the 12-ane- S_4 complex, the latter two complexes involving a single coordinated apical water. For the 15-ane- S_5 complex the Cu(II) is coordinated to all five sulfur donor atoms in a square-pyramidal array: (a) Pett, V. B. Ph.D. Dissertation, Wayne State University, 1979. (b) Pett, V. B.; Dockal, E. R.; Diaddario, L. L.; Glick, M. D.; Corfield, P. W. R.; Rorabacher, D. B., to be submitted for publication.

This structural change may also account for the slight aberration in the trend in ΔS° values which occurs at this point.

The observation that the open-chain ligand complex $\text{Cu}(\text{Me}_2\text{-}2,3,2\text{-S}_4)$ exhibits a ΔH° value which is identical with that for the complex with the 14-ane- S_4 ligand illustrates the fallacy in the earlier claim⁴ that such cyclic ligand species would form stronger coordinate bonds than would their open-chain counterparts. In fact, the difference in ΔH° values for the $\text{Me}_2\text{-}$ and $\text{Et}_2\text{-}2,3,2\text{-S}_4$ complexes reflects the fact that the ethyl groups in the latter complex encounter steric problems, resulting in a slightly nonplanar coordination of one terminal sulfur donor atom as revealed in the resolved crystal structure.^{14,19}

A comparison of the thermodynamic values exhibited by the $\text{Cu}(\text{II})$ complexes with 15-ane- S_4 and 15-ane- S_5 is also of interest. The latter ligand bonds all five sulfur donors to the $\text{Cu}(\text{II})$ ion, resulting in greater internal strain within the complexed ligand. This may account for the reasonably constant ΔH° value for the two complexes despite the extra Cu-S bond formed with the pentathia ether ligand. The significantly larger ΔS° value for the latter ligand is contrary to the greater rigidity experienced by this ligand upon complexation and is clearly a reflection of the entropy contribution resulting from complete desolvation of $\text{Cu}(\text{II})$ in this complex.

Conclusions

The following general conclusions are consistent with the experimentally evaluated stability constant values for the $\text{Cu}(\text{II})$ -polythia ether complexes.

(1) Increasing the concentration of HClO_4 in the solvent medium results in a marked increase in the apparent stability

constant values for the $\text{Cu}(\text{II})$ -polythia ether complexes. As evaluated for $\text{Cu}(\text{II})(14\text{-ane-S}_4)$ in aqueous solution, the increase in the apparent stability constant at 25 °C amounts to approximately 2-fold, 5-fold, and 17-fold for solutions containing 0.10, 0.50, and 1.00 M HClO_4 , respectively. This stability constant increase is consistent with a model in which perchlorate ion forms a tight ion pair (or a ternary complex) with the $\text{Cu}(\text{II})$ -polythia ether complexes for which the 25 °C activity equilibrium constant value is 24 M^{-1} .

(2) With the assumption that the perchlorate ion effect is roughly equivalent for all of the $\text{Cu}(\text{II})$ -polythia ethers studied, the entropy of complex formation is seen to steadily decrease as the ring size of the ligand increases from 12-ane- S_4 ($\Delta S^\circ = +15.9 \text{ eu}$) to the open-chain species ($\Delta S^\circ = -5.4$ and -2.5 eu) with a slight discontinuity for 16-ane- S_4 . The fact that the maximum stability occurs with the 14-ane- S_4 ligand complex is attributable to the overriding favorable enthalpy which correlates to the optimal coordination geometry (shortest Cu-S bond lengths combined with planar coordination as revealed from crystallographic studies).

(3) The value of ΔH° for the open-chain ligand complexes is virtually identical with that obtained for the complex involving the optimally fitting cyclic ligand 14-ane- S_4 . Thus, the *macrocyclic effect* is wholly attributable to the *more favorable entropy* associated with the less flexible cyclic ligand.

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Registry No. Cu , 7440-50-8; HClO_4 , 7601-90-3; 12-ane- S_4 , 25423-56-7; 13-ane- S_4 , 25423-54-5; 14-ane- S_4 , 24194-61-4; 15-ane- S_4 , 57704-75-3; 16-ane- S_4 , 295-91-0; 15-ane- S_5 , 36338-04-2; $\text{Me}_2\text{-}2,3,2\text{-S}_4$, 25676-65-7; $\text{Et}_2\text{-}2,3,2\text{-S}_4$, 57704-77-5.

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Electrochemical and NMR Studies of Six-Coordinate Oxidized μ -Nitrido Iron Porphyrin Dimers

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The reaction of μ -nitrido-bis[(5,10,15,20-tetraphenylporphyrinato)iron] cation with aniline and 11 substituted pyridines in the solvent 1,2-dichloroethane was studied electrochemically. Half-wave potential shifts as a function of added ligand concentration indicated that bisligated adducts of the oxidized μ -nitrido dimer were formed in solution. For the ligands investigated, the magnitude of the formation constants ranged from $10^{3.8}$ to $10^{8.6}$. A plot of $\log \beta_2$ vs. $\text{p}K_a$ of the added ligand suggests that σ bonding is the predominant mode of ligand to metal interaction. A common dimeric product is produced by either one-electron chemical or electrochemical oxidation of the parent μ -nitrido complex. Nuclear magnetic resonance spectroscopy has been utilized to characterize the oxidized product. Bisligation of nitrogenous bases to the oxidized dimeric product has been unequivocally demonstrated. Tentative evidence for monoligation at low temperatures is presented.

Introduction

The synthesis³ as well as the molecular structure⁴ of μ -nitrido-bis[(5,10,15,20-tetraphenylporphyrinato)iron], $(\text{TPP-Fe})_2\text{N}$, has been recently reported. Comparisons of the physical properties of this complex with similar compounds were difficult as this was the first example of two first-row

transition-metal atoms being bridged with a single nitrogen atom. Other dimeric μ -nitrido species have been reported,⁵ but these complexes contain second- and third-row transition metals. Recently, we have reported XPS results⁶ which are consistent with the presence of two equivalent, *low-spin* iron atoms in this dimer. This would be only the second case⁷ of a five-coordinate iron porphyrin complex given the low-spin

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