well have significant inner-sphere character. Thus the present reaction, oxidation of NO by $[Ni(tacn)_2]^{3+}$, appears to be the best candidate for discussion as an example of outer-sphere electron transfer involving the NO^+/NO redox couple.

An analysis of the rate constant for the outer-sphere reaction of NO with $[Ni(tacn)_2]^{3+}$ in terms of the cross-relationship of Marcus' theory, as in eqs 8-11, leads to a value of 5 M^{-1} s^{-1} for the effective self-exchange rate constant of the NO^+/NO system. For this analysis, a value of 1.77 Å was selected as the radius of NO and NO^+. It is inappropriate to give extensive discussion to the magnitude of this self-exchange rate constant until the result is confirmed with other oxidants. However, the low value does imply a significant barrier, and it is qualitatively consistent with the predictions of Eberson and Radner[33] and the electrochemical kinetics results of Lee, Kuchynka, and Kochi.[34]

Conclusions. Nitrite is oxidized by $[Ni(tacn)_2]^{3+}$ with rate-limiting electron transfer. This result, combined with a slightly revised potential for the NO_2/NO_2^- couple, leads to a revised estimate of the effective self-exchange rate constant for the NO_2/NO_2^- couple. The reaction of NO with $[Ni(tacn)_2]^{3+}$ is unique in the chemistry of this coordination compound, since it can lead to destruction of the complex via its conjugate-base form. In highly acidic media there is a direct reaction between NO and $[Ni(tacn)_2]^{3+}$, and this is interpreted as the first example of outer-sphere electron transfer from NO in homogeneous solution.

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Macrocyclic Polyamino Polythiaether Ligands with N_xS_{4-x} and N_xS_{5-x} Donor Sets: Protonation Constants, Stability Constants, and Kinetics of Complex Formation with the Aquocopper(II) Ion

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The entire series of 14-membered macrocyclic ligands containing the N_xS_{4-x} donor set (where x = 1, 2, 3) with alternating ethylene and propylene bridging groups and two related 15-membered macrocycles with the N_xS_{5-x} donor set (where x = 1, 2) containing only ethylene bridging groups have been characterized in terms of their protonation constants, Cu(II) complex stability constants, and complex formation kinetics with aquocopper(II) ion in aqueous solution at 25 °C. These data are compared to the properties of the corresponding homoleptic ligands [14]aneS$_4$, [14]aneN$_4$ (i.e., cyclam), [15]aneS$_5$, and [15]aneN$_5$ in an attempt to shed further light on the effects of ligand cyclization upon the thermodynamics and the mechanism of metal complex formation. The logarithmic values of the aqueous mixed-mode protonation constants (defined as $K_{Hn}^m = [H_nL^{n+}]/a_H[H_{n-1}L^{(n-1)+}]$) at 25 °C, μ = 0.10 M, are as follows (listed in the order log K_{H1}^m and, where applicable, log K_{H2}^m, log K_{H3}^m; values in parentheses represent standard deviations within a single determination, while italicized values in braces represent standard deviations among several *replicate* determinations): [14]aneNS$_3$, 8.75 (±0.02); [14]aneN$_2$S$_2$, 9.41 {*±0.23*}, 5.69 {*±0.34*}; [14]aneNSSN, 9.71 {*±0.17*}, 6.60 {*±0.14*}; [14]aneNSNS, 9.78 (±0.12), 8.16 (±0.08); [14]aneN$_3$S, 9.66 (±0.08), 8.24 (±0.12), 2.53 (±0.02); [15]aneNS$_4$, 8.14 (±0.07); [15]aneN$_2$S$_3$, 8.70 (±0.01), 5.16 (±0.01). The corresponding logarithmic stability constants for the $Cu^{II}L$ complexes (log $K_{Cu^{II}L}$) are as follows: [14]aneNS$_3$, 9.25; [14]aneN$_2$S$_2$, 15.26; [14]aneNSSN, 15.72; [14]aneNSNS, 15.15; [14]aneN$_3$S, >18; [15]aneNS$_4$, 9.80; [15]aneN$_2$S$_3$, 16.02. The specific rate constants for the reaction of aquocopper(II) ion with the various protonated ligand species were resolved as follows (listed in the order k_{Cu}^L, k_{Cu}^{HL}, and, where applicable, $k_{Cu}^{H_2L}$, the superscript indicating the degree of protonation of the ligand; all values in M^{-1} s^{-1}): [14]aneNS$_3$, (3.2 ± 0.2) × 10^6, (1.4 ± 0.3) × 10^2; [14]aneN$_2$S$_2$, (1.6 ± 0.1) × 10^8, (1.3 ± 0.6) × 10^3; [14]aneNSSN, (8.2 ± 0.6) × 10^7, (5 ± 2) × 10^3; [14]aneNSNS, (2.0 ± 0.4) × 10^9, (2.9 ± 0.7) × 10^5; [14]aneN$_3$S, k_{Cu}^L not evaluated, (3.1 ± 0.1) × 10^5, 51 ± 13; [15]aneNS$_4$, (8.4 ± 0.4) × 10^6, (1.4 ± 0.3) × 10^3; [15]aneN$_2$S$_3$, (8 ± 2) × 10^7, (2.5 ± 0.1) × 10^5. For unprotonated ligands containing a single nitrogen donor atom, the rate-determining step in the complex formation with aquocopper(II) ion comes at the point of the first coordinate bond formation involving a nitrogen donor atom, with the values being essentially identical with those for corresponding open-chain ligands. This implies that the increased stability constants commonly observed for macrocyclic ligand complexes arise directly from a reduction of the dissociation rate constants. In the case of monoprotonated ligand species, the complex formation rate constants are generally much smaller than corresponding open-chain species, although this effect varies by several orders of magnitude for ligands with the same donor set, depending upon the specific arrangement of the donor atoms within the macrocyclic ring. The results of the current studies indicate that the reaction kinetics of the unprotonated, mono- and diprotonated species of macrocyclic ligands yield differing information about the fundamental mechanistic consequences of simple ligand cyclization.

Introduction

The enhanced stability of metal ion complexes formed with macrocyclic ligands compared to those formed with analogous open-chain species has been termed the "macrocyclic effect"[2] and has sparked much interest in the study of cyclic ligand complexes. Thermodynamic studies indicate that these stability constant differences arise primarily from two properties associated with the *uncomplexed* macrocyclic ligands: (i) the diminished flexibility of free macrocyclic ligands, resulting in a less negative *entropy* term upon complexation[2-4] and, (ii) in the case of ligands with hydrogen-bonding donor atoms in protolytic solvents, the diminished solvation of the free macrocyclic ligands relative to their

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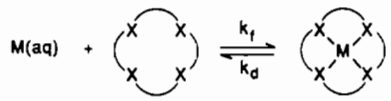
open-chain counterparts, resulting in a more favorable *enthalpy* term upon complexation.[2,5]

Macrocyclic Kinetic Effects. Kinetic measurements provide additional insight into the nature of the macrocyclic effect. Both metal complex formation and dissociation kinetics are expected to be affected by ligand cyclization as a result of decreased conformational flexibility. Kinetic studies on saturated, unsubstituted, macrocyclic ligands reacting with aquometal ions (eq 1)



(1)

have been carried out on several different ligand types in an attempt to elucidate the detailed reaction mechanisms involved in inserting the metal ion into the ligand cavities.[6] The majority of these studies have employed homoleptic ligands, i.e., ligands with uniform donor atoms (X = O, N, or S). Analysis of the macrocyclic effect in terms of the stepwise mechanistic processes has generally been ambiguous due to specific experimental limitations associated with each type of ligand.

Studies on ligands containing only ether oxygen donor atoms (crown ethers) have primarily been limited to reactions with alkali-metal ions and related cationic species whose inner hydration shells are too labile to permit discrimination among the stepwise substitution processes.[7-10] In the case of ligands with all amine nitrogen donors (cyclic polyamines), the strongly basic character of the nitrogens leads to extensive ligand protonation at pH values accessible to most aquometal ions. As a result, specific formation rate constants can be obtained only for the mono- and diprotonated species.[11-13] Interpretation of these latter rate constants is complicated both by electrostatic interactions between the positively charged metal ions and the positively charged protonated ligand species and by the strong tendency of the protonated cyclic polyamine species either to form internal hydrogen bonds or to form hydrogen bonds with the solvent, both of which may shift the conformational equilibria toward unreactive "endo" conformers.[14] Some kinetic studies have been conducted at very high pH (13 to >14) on unprotonated macrocyclic polyamine ligands reacting with $Cu(OH)_3^-$ and $Cu(OH)_4^{2-}$.[15] Unfortunately, no comparable kinetic information has been generated for other complexation reactions involving these hydroxocopper species so that some ambiguity remains regarding the position of the rate-determining step.

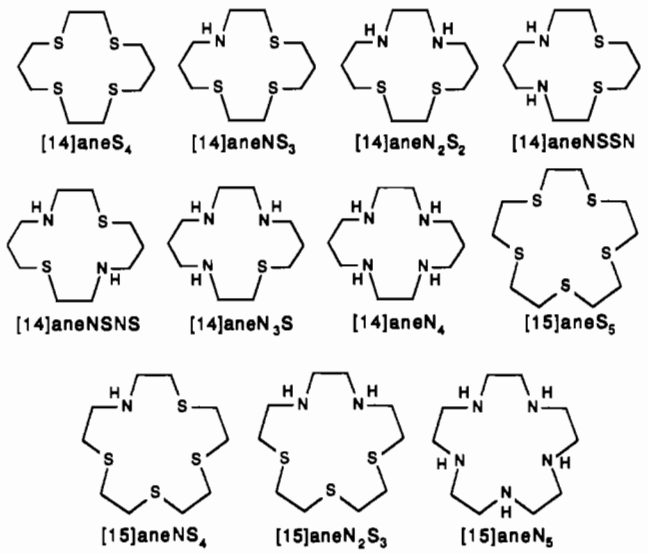


Figure 1. Macrocyclic polyamino polythiaether ligands studied in this work and related polythiaether and polyamine ligands to which they are compared.

Kinetic studies using polythiaether ligands reacting with solvated Cu(II) have also made it possible to eliminate the problems associated with ligand protonation, but the limited solubility of these ligands in aqueous solution necessitated the use of methanol–water mixtures for the solvent matrix. Rigorous mathematical extrapolations to aqueous conditions have been made by varying the solvent composition for an entire series of homologous cyclic and open-chain polythiaether ligands.[16] Such extrapolations have been supported by the direct determination in aqueous solution of the complex formation rate constant for the aquocopper(II) ion reacting with the 15-membered cyclic tetrathiaether ligand ([15]-aneS$_4$)[16] and with water-soluble polythiaether derivatives.[17] In all polythiaether ligand complexation reactions studied to date, however, the rate-determining step appears to be at the point of second bond formation, making it impossible to assess the effect of ligand cyclization upon the initial bonding step.

Studies on Macrocycles with Mixed N–S Donors. To circumvent most of the foregoing difficulties and to provide unique comparative information on the cyclization mechanism, we have now undertaken a thorough study of the thermodynamics and kinetics of reactions involving the family of cyclic ligands containing all possible combinations of amine nitrogen and thiaether sulfur donor atoms within a uniform macrocyclic skeletal framework. (Although a number of previous studies have been reported on macrocyclic ligands with N–S donors, most have been devoid of kinetic measurements.)[18,19] The aquocopper(II) ion

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has been selected as the coordinating metal ion on the basis of its ability to form coordinate bonds of measurable stability with both of these donor atom types. To achieve an optimal fit of the ligand cavity to the encapsulated metal ion, we have utilized the 14-membered quadridentate macrocyclic skeleton, involving alternating ethylene and propylene bridging groups. Also included for comparison are two similar quinquedentate 15-membered macrocyclic ligands, having all-ethylene bridging groups. All of these ligands are sufficiently soluble to permit their study directly in aqueous media. For all seven polyamino polythiaether macrocycles, we have determined (i) the ligand mixed-mode protonation constants (K_{H1}^m, K_{H2}^m, K_{H3}^m), (ii) the Cu(II) complex stability constants ($K_{Cu^{II}L}$), and (iii) the rate constants for these ligands reacting with aquocopper(II) ion in aqueous solution:

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

In this reaction, L′ represents the sum of all protonated and unprotonated forms of the uncomplexed ligand, and $Cu^{II}L'$ represents all forms of the copper(II) complex (vide infra). Specific rate constants have been resolved by varying the pH for the various unprotonated and protonated ligand species.

The seven macrocyclic ligands investigated in this study include 1,4,8-trithia-11-azacyclotetradecane ([14]aneNS$_3$), 1,4-dithia-8,11-diazacyclotetradecane ([14]aneN$_2$S$_2$), 1,11-dithia-4,8-diazacyclotetradecane ([14]aneNSSN), 1,8-dithia-4,11-diazacyclotetradecane ([14]aneNSNS), 1-thia-4,8,11-triazacyclotetradecane ([14]aneN$_3$S), 1,4,7,10-tetrathia-13-azacyclopentadecane ([15]aneNS$_4$), and 1,4,7-trithia-10,13-diazacyclopentadecane ([15]aneN$_2$S$_3$). Of these ligands, only [14]aneN$_2$S$_2$ has been previously studied.[19] All seven ligands are depicted in Figure 1, along with their homoleptic analogues.

In terms of mechanistic arguments, the two ligands of greatest interest are those containing one amine nitrogen donor atom with weakly bonding thiaether sulfurs occupying the remainder of the donor sites, that is, [14]aneNS$_3$ and [15]aneNS$_4$. For the unprotonated species, the lone nitrogen donor atom is of sufficient bonding strength to enhance the probability that first bond formation will be the rate-determining step; and the presence of only a single basic donor atom eliminates the possibility of the accelerative kinetic behavior associated with diamines and higher polyamines, which results from hydrogen bonding by the ligand to a coordinated water molecule at the time of first bond formation (the *internal conjugate base* (ICB) effect).[20,21] Thus, these two ligands give the most unambiguous mechanistic information yet achieved regarding the effect of ligand cyclization on the rate constant for complex formation. For the other species studied, comparisons of the rate constants obtained as a function of ligand protonation, number of nitrogen donor atoms, and the arrangement of N and S donor atoms can generally be explained in terms of (i) the position of the rate-determining step, (ii) ligand conformational effects, and (iii) outer-sphere hydrogen bonding effects. Several interesting effects of cyclization upon the kinetics are noted.

As might be anticipated, the macrocyclic polyamino polythiaether ligands exhibit an interesting range of properties intermediate between those of the macrocyclic polythiaethers and the macrocyclic polyamines. The specific trends in their protonation constants and Cu(II) complex stability constants suggest, in fact, that these ligands should provide a variety of interesting chemical behaviors worthy of further exploitation.

Experimental Section

Reagents. The preparation and purification of $Cu(ClO_4)_2$ and $NaClO_4$ (used for ionic strength control) and the standardization of Cu(II) have been previously described.[17] The synthetic methods for preparing the various macrocyclic polyamino polythiaether ligands will be published separately.[22] All ligands were obtained in the form of either the free amine or the hydrochloride salt. Solutions of the polyamino polythiaether ligands were standardized spectrophotometrically by adding a large excess of aquocopper(II) ion and/or by potentiometric titration of the acidified ligand solutions with NaOH. Protonation constants for all ligands included in this work were determined by potentiometric titration of the protonated species with standardized carbonate-free NaOH solution. In all cases, excess $HClO_4$ was added to the ligand solution to ensure that the ligand was fully protonated prior to the start of the titration. The ionic strength was maintained at 0.10 M by adding appropriate amounts of $NaClO_4$ to both the titrant and ligand solutions. Conductivity grade distilled–deionized water was used to prepare all solutions. For the kinetic measurements, solutions were buffered with approximately 5×10^{-3} M boric acid (reagent grade, Fisher Scientific Co.), half-neutralized with NaOH, to which was added a variable amount of mannitol to achieve the desired pH level.

Instrumental Methods. Absorbance measurements for the determination of spectra, molar absorptivity values, ligand concentration, and stability constants and for the slower kinetic measurements were made with a Cary 17D double-beam recording spectrophotometer. A temperature of 25.0 ± 0.1 °C was maintained by circulating water from a Forma Scientific Model 1095 refrigerated water bath through a specially constructed thermostated cell holder. All other kinetic measurements were made with a thermostated Durrum D-110 stopped-flow spectrophotometer interfaced to a Data General NOVA 3 minicomputer, as previously described.[17] The data were then transferred to a Data General Eclipse 5/130 computer for final resolution of the observed rate constants. All stopped-flow measurements were made at 25.0 ± 0.2 °C. Titrations were carried out in a closed vessel with humidified nitrogen passed over the solution to prevent CO_2 absorption, and the solution was maintained at 25.0 ± 0.1 °C. All potentiometric titrations were followed with an Orion 901 microprocessor ionalyzer equipped with an Orion Research Ross combination pH electrode. The Ross electrode was filled with 3 M NaCl rather than KCl to prevent possible precipitation of $KClO_4$ at the liquid junction.

Results

Protonation Constants. For the ligands included in this work, there are a maximum of three protonation constants represented by the following reactions:

$$L + H^+ \rightleftharpoons HL^+ \qquad (3)$$

$$HL^+ + H^+ \rightleftharpoons H_2L^{2+} \qquad (4)$$

$$H_2L^{2+} + H^+ \rightleftharpoons H_3L^{3+} \qquad (5)$$

The protonation constants were treated as mixed-mode values, as defined by the relationships

$$K_{H1}^m = [HL^+]/a_H[L] \qquad (6)$$

$$K_{H2}^m = [H_2L^{2+}]/a_H[HL^+] \qquad (7)$$

$$K_{H3}^m = [H_3L^{3+}]/a_H[H_2L^{2+}] \qquad (8)$$

where a_H represents the activity of the hydrogen ion as calculated from the pH. The values of these constants were calculated from the titrimetric data by using an approach similar to (but more rigorous than) Jonassen's modification[23] of Bjerrum's $\bar{n}_H$ method.[24] In this approach, $\bar{n}_H$ is defined as the average number of ionizable hydrogens attached to the ligand, viz.,

$$\bar{n}_H = ([HL^+] + 2[H_2L^{2+}] + 3[H_3L^{3+}])/[L'] \qquad (9)$$

where [L′] is defined by the relationship

$$[L'] = [L] + [HL^+] + [H_2L^{2+}] + [H_3L^{3+}] \qquad (10)$$

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Table I. Experimental Protonation Constant Data for [14]aneN$_2$S$_2$ and [14]aneNSSN in Aqueous Solution at 25 °C, μ = 0.1 M ($NaClO_4$)[a]

ligand	log K_{H1}^m	log K_{H2}^m
[14]aneN$_2$S$_2$	9.70 (1)	5.58 (2)
	9.61 (7)	6.07 (3)
	9.58 (1)	5.34 (1)
	9.38 (14)	6.07 (5)
	9.29 (11)	5.89 (4)
	9.27 (3)	5.22 (1)
	9.06 (9)	5.69 (4)
mean	9.41 {23}	5.69 {34}
[14]aneNSSN	9.88 (2)	6.53 (5)
	9.83 (9)	6.80 (8)
	9.60 (7)	6.59 (1)
	9.54 (5)	6.49 (1)
mean	9.71 {17}	6.60 {14}

[a] In this and all subsequent tables, the values listed in parentheses represent the standard deviation values based on the consistency of the data within a single determination, the digits listed referring to the significant figures furthest to the right in the preceding quantities: e.g., 9.06 (9) represents 9.06 ± 0.09. Values in braces represent the corresponding standard deviation values for the means of several replicate determinations.

For solutions initially containing the fully protonated ligand to which both excess strong acid and strong base have been added, the $\bar{n}_H$ relationship may be calculated from the expression[24]

$$\bar{n}_H = (C_H - C_{OH} + [OH^-] - [H^+])/[L'] \quad (11)$$

where C_H is the concentration of excess acid, C_{OH} is the total concentration of NaOH added at any point, $[H^+] = 10^{-pH}/\gamma_H$, $[OH^-] = K_w/(10^{-pH}\gamma_{OH})$, $K_w = 10^{-14.00}$ (at 25 °C), and γ_H and γ_{OH} are the respective activity coefficients for H^+ and OH^- calculated by using the extended Debye–Hückel equation. In all cases, the initial concentration of the ligand was determined spectrophotometrically by complexation with excess Cu(II) to minimize any uncertainty in the value of [L'].

The following relationships for the mixed-mode protonation constants can be obtained by combining eqs 6–10 (avoiding Jonassen's simplifying assumptions):[23]

$$K_{H1}^m = \frac{\bar{n}_H}{(1 - \bar{n}_H)a_H + (2 - \bar{n}_H)K_{H2}^m(a_H)^2 + (3 - \bar{n}_H)K_{H2}^m K_{H3}^m(a_H)^3} \quad (12)$$

$$K_{H2}^m = \frac{\bar{n}_H + (\bar{n}_H - 1)K_{H1}^m a_H}{(2 - \bar{n}_H)K_{H1}^m(a_H)^2 + (3 - \bar{n}_H)K_{H1}^m K_{H3}^m(a_H)^3} \quad (13)$$

$$K_{H3}^m = \frac{\bar{n}_H + (\bar{n}_H - 1)K_{H1}^m a_H + (\bar{n}_H - 2)K_{H1}^m K_{H2}^m(a_H)^2}{(3 - \bar{n}_H)K_{H1}^m K_{H2}^m(a_H)^3} \quad (14)$$

With application of eq 12 to the titrimetric data obtained in the range $0.2 < \bar{n}_H < 0.8$ (and, where applicable, eq 13 in the range $1.2 < \bar{n}_H < 1.8$ and eq 14 in the range $2.2 < \bar{n}_H < 2.8$), all of the protonation constants for each specific ligand were evaluated by initially assuming that the unknown K_{Hn}^m terms on the right side of eqs 12–14 were negligible and then using an iterative computer program to obtain corrected values.

For the ligands containing only one or two nitrogen donor atoms, limited ligand solubility required operating at ligand concentrations of 10^{-3}–10^{-4} M. In the case of systems involving multiple protonation constants, these low concentrations (and, possibly, other unidentified contributing factors) markedly affected the reproducibility of the protonation constant determinations. The [14]aneN$_2$S$_2$ ligand, for which concentrations were limited to (1–2) × 10^{-4} M, was the most seriously affected, and several titrations were carried out on this ligand (involving multiple individual workers). Similar repetitive determinations were made on [14]aneNSSN, where concentration levels of (2–4) × 10^{-3} M were achievable. The resolved protonation constant values obtained from each of the determinations on these two ligands are listed in Table I. The mean values from this table, along with values obtained from the best of several single determinations on the remaining five ligands (and relevant literature values), are presented in Table II. These K_H^m values were used for all subsequent calculations involving the complex stability constants and the resolved formation rate constants. (Note: Despite the unsatisfactory precision, the protonation constants for [14]aneN$_2$S$_2$ appear to be known within about a factor of 2, which should not affect the subsequent interpretation of the kinetic data.)

Table II. Resolved Protonation Constant Values for Macrocyclic Polyamino Polythiaether Ligands in Aqueous Solution at 25 °C, μ = 0.1 M ($NaClO_4$)[a]

ligand	log K_{H1}^m	log K_{H2}^m	log K_{H3}^m	log K_{H4}^m	log K_{H5}^m
Quadridentate Macrocycles					
[14]aneNS$_3$	8.75 (2)				
[14]aneN$_2$S$_2$	9.41 {23}[b]	5.69 {34}[b]			
	[9.77, 9.75][c]	[5.72, 6.01][c]			
[14]aneNSSN	9.71 {17}[b]	6.60 {14}[b]			
[14]aneNSNS	9.78 (12)	8.16 (8)			
[14]aneN$_3$S[d]	9.66 (8)	8.24 (12)	2.53 (2)		
[14]aneN$_4$	[11.50][e]	[10.30][e]	[1.62][e]	[0.94][e]	
	[11.83][f]	[10.76][f]	[<2][f]	[<2][f]	
Quinquedentate Macrocycles					
[15]aneNS$_4$	8.14 (7)				
[15]aneN$_2$S$_3$	8.697 (4)	5.16 (1)			
[16]aneN$_2$SN$_2$[g]	*[9.33]*[g]	*[8.85]*[g]	*[4.49]*[g]	*[3.2]*[g]	
[16]aneN$_5$[g]	*[10.64]*[g]	*[9.49]*[g]	*[7.28]*[g]	*[1.7]*[g]	*[1.5]*[g]
[15]aneN$_5$	[10.85][h]	[9.65][h]	[6.00][h]	[1.74][h]	[1.16][h]

[a] Values in square brackets are from the literature; all others are from the current study. [b] Mean values from repetitive determinations as listed in Table I. [c] Reference 19a (in 2% (v/v) CH_3CN, 20 °C, μ = 0.2 M (KNO_3)). [d] A total of four titrations were run on the [14]aneN$_3$S ligand with similar results; only one determination was carried out under optimal conditions, however, and the results from that determination are reported here. [e] Ref 11c (μ = 0.2 M). [f] Reference 13f (μ = 0.5 M (KNO_3)). [g] The two ligands listed in italics are 16-membered macrocyclic quinquedentate ligands that are closely related to the 15-membered ligands considered here: reference 18b (μ = 0.2 M). [h] Reference 11d (μ = 0.2 M).

Stability Constants of Copper(II)–Polyamino Polythiaether Complexes. Since all of the polyamino polythiaether ligands are relatively basic, the ligands are highly protonated at lower pH values (<5.5) where hydroxocopper(II) species have been shown to be insignificant.[17] After several possible methods were investigated for determining the Cu(II) complex stability constants, the method finally adopted in this work was to determine $K_{Cu^{II}L'}$ (eq 15) by means of the spectrophotometric method of McConnell

$$K_{Cu^{II}L'} = [Cu^{II}L']/[Cu^{II'}][L'] \quad (15)$$

and Davidson,[25] which we have previously utilized for the Cu(II) polythiaether complexes.[3,26] (This method is applicable to weak complexes with strong absorption bands and can be applied to the current systems by selecting a low pH value where $10^2 < K_{Cu^{II}L'} < 10^6$.) In eq 15, $[Cu^{II}L']$ and $[Cu^{II'}]$ represent the summation of the concentrations of all species of Cu(II) that are complexed and uncomplexed by the macrocyclic ligand, respectively, i.e.,

$$[Cu^{II}L'] = [Cu^{II}L^{2+}] + [Cu^{II}LX^+] + [Cu^{II}HL^{3+}] + [Cu^{II}(OH)L^+] + \ldots \quad (16)$$

$$[Cu^{II'}] = [Cu^{2+}] + [Cu^{II}OH^+] + 2[Cu^{II}_2(OH)_2^{2+}] + \ldots \quad (17)$$

At the low pH levels used in this study, none of the hydroxo-

(25) McConnell, H.; Davidson, N. *J. Am. Chem. Soc.* **1950**, *72*, 3164–3167. The spectrophotometric method described was first proposed by: Benesi, H. A.; Hildebrand, J. H. *Ibid.* **1949**, *71*, 2703–2707.
(26) Young, I. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1986**, *25*, 2576–2582.
(27) Ringbom, A. *Complexation in Analytical Chemistry*; Wiley-Interscience: New York, 1963.

Table III. Experimental Conditional Stability Constants and Calculated Thermodynamic Stability Constant Values for the Copper(II) Complexes Formed with Macrocyclic Polyamino Polythiaethers in Aqueous Solution at 25 °C, μ = 0.10 M ($NaClO_4$)

complexed ligand	pH	α_L	$K_{CuL'}$, M^{-1}	log $K_{CuL''}$
		Quadridentate Macrocycles		
[14]aneS$_4$	1.0	1.00	2.18 (3) × 10^{4} [a]	4.34[a]
[14]aneNS$_3$	2.8	8.91 × 10^{5}	1.99 (2) × 10^{3}	9.25
[14]aneN$_2$S$_2$	1.7	5.0 × 10^{11}	3.62 (10) × 10^{3}	15.26
				[15.85][b]
[14]aneNSSN	2.3	5.0 × 10^{11}	1.07 (3) × 10^{4}	15.72
[14]aneNSNS	2.7	3.6 × 10^{12}	3.94 (36) × 10^{2}	15.15
[14]aneN$_3$S	2.7	4.21 × 10^{12}	$\gg$1 × 10^{5}	$\gg$18 ($\approx$20)[c]
[14]aneN$_4$				[27.2][d]
		Quinquedentate Macrocycles		
[15]aneS$_5$	1.0	1.00	1.53 (2) × 10^{4} [a]	4.18[a]
[15]aneNS$_4$	2.2	8.71 × 10^{5}	7.24 (11) × 10^{3}	9.80
[15]aneN$_2$S$_3$	1.0	7.19 × 10^{11}	1.44 (3) × 10^{4}	16.02[e]
[16]aneN$_4$S				*[24.14]*[f]
[16]aneN$_5$				*[27.10]*[f]
[15]aneN$_5$				[28.3][g]

[a] Reference 3. [b] Reference 19a (20 °C, μ = 0.2 M). [c] Value in parentheses is interpolated from other data in this table (see text). [d] Reference 11b (μ = 0.2 M). [e] Possibly too high due to the failure to correct for the formation of the protonated species of the complex, $CuHL^+$ (see text and ref 30). [f] The two ligands listed in italics are 16-membered macrocyclic quinquedentate ligands that are closely related to the 15-membered ligands considered here: reference 18b (μ = 0.2 M). [g] Reference 11d (μ = 0.2 M).

copper(II) species is present in significant concentration and $[Cu^{II\prime}] \approx [Cu^{2+}]$.[28] Of the possible $Cu^{II}L$ species, hydroxo species such as $Cu^{II}(OH)L^+$ should also be insignificant under these conditions. Independent electrochemical studies indicate that protonated species, such as $Cu^{II}HL^{3+}$, are insignificant down to pH 2.0 or below for the complexes studied here[29] (with the possible exception of [14]aneN$_3$S). Thus, only the first two terms on the right side of eq 16 were considered, where $Cu^{II}LX^+$ represents a perchlorate adduct (vide infra).

Once the conditional stability constant, $K_{Cu^{II}L'}$, has been evaluated, the value of the thermodynamic stability constant, $K_{Cu^{II}L}$, can be calculated according to the relationship

$$K_{Cu^{II}L} = [CuL^{2+}]/[Cu^{2+}][L] = K_{Cu^{II}L'}\alpha_L\alpha_{Cu^{II}}/\alpha_{Cu^{II}L} \quad (18)$$

where the α values have been defined (using Ringbom's convention)[27] respectively as the reciprocal fractions of the uncomplexed, unprotonated ligand, the aquocopper(II) ion, and the $Cu^{II}L$ complex devoid of protonation and hydroxide complexation, as defined by the following relationships:

$$\alpha_L = [L']/[L] = ([L] + [HL^+] + [H_2L^{2+}] + [H_3L^{3+}])/[L] = 1 + K_{H1}{}^{m}a_H + K_{H1}{}^{m}K_{H2}{}^{m}(a_H)^2 + K_{H1}{}^{m}K_{H2}{}^{m}K_{H3}{}^{m}(a_H)^3 \quad (19)$$

$$\alpha_{Cu^{II}} = [Cu^{II\prime}]/[Cu^{2+}] \approx 1 \quad (20)$$

$$\alpha_{Cu^{II}L} = [Cu^{II}L']/[Cu^{II}L^{2+}] \approx ([Cu^{II}L^{2+}] + [Cu^{II}LX^+])/[Cu^{II}L^{2+}] \quad (21)$$

Evidence for a perchlorate adduct, $Cu^{II}LX^+$, has been found for a variety of Cu(II) polythiaether complexes,[3,26] suggesting that this species may represent approximately two-thirds of the total $Cu^{II}L$ complex in 0.10 M $NaClO_4$. Since the perchlorate adducts have properties virtually identical with those of the $Cu^{II}L^{2+}$ species and the extent of adduct formation has not been evaluated in the case of the polyamino polythiaether complexes, corrections for the perchlorate adduct were not made in the course of this investigation. Thus, the Cu(II) complex stability constants have been resolved in terms of a modified thermodynamic stability constant, $K_{Cu^{II}L''}$

$$K_{Cu^{II}L''} = [Cu^{II}L']/[Cu^{2+}][L] = K_{Cu^{II}L}\alpha_{Cu^{II}L} = K_{Cu^{II}L'}\alpha_L \quad (22)$$

where $K_{Cu^{II}L''}$ is seen to differ from the thermodynamic stability constant, $K_{Cu^{II}L}$, only by the inclusion of the perchlorate adduct of the copper complex, $Cu^{II}LX^+$.[30] These modified thermodynamic stability constant values, obtained for all systems by using the foregoing procedure, are listed in Table III. (Since other investigators have not taken anion adducts into account, the $K_{Cu^{II}L''}$ values reported here are equivalent to $K_{Cu^{II}L}$ values found in the literature.)[19]

Table IV. Characteristic Spectral Bands for Copper(II) Complexes with Macrocyclic Polythiaethers and Polyamino Polythiaethers in Aqueous Solution at 25 °C

complexed ligand	λ_1(max), nm	ϵ_{CuL} × 10^{-3}, M^{-1} cm^{-1}	λ_2(max), nm	ϵ_{CuL} × 10^{-3}, M^{-1} cm^{-1}
	Quadridentate Macrocycles			
[14]aneS$_4$	390[a]	8.0 (1)[a]	570[a]	1.9 (1)[a]
[14]aneNS$_3$	365	7.7 (1)	550	1.0 (1)
[14]aneN$_2$S$_2$	337	7.6 (1)	530	0.78 (1)
	[335][b]	[9.5][b]	[531][b]	[0.386][b]
[14]aneNSSN	335	7.3 (1)	530	0.64 (1)
[14]aneNSNS	356	7.8 (1)	545	0.78 (1)
[14]aneN$_3$S	315	3.9 (1)	510	0.33 (1)
[14]aneN$_4$	255	8.2 (1)	500	0.09 (1)
	Quinquedentate Macrocycles			
[15]aneS$_5$	414[a]	6.1 (1)[a]	565[a]	0.20 (1)[a]
[15]aneNS$_4$	414	6.1 (1)	565	0.19 (1)
[15]aneN$_2$S$_3$	352	6.5 (1)	550	0.38 (1)
[15]aneN$_5$	[275][c]	[5.5][c]	[585][c]	[0.20][c]

[a] Reference 31. [b] Reference 32. [c] Reference 33.

Spectral Characteristics. In the course of determining the stability constants for the $Cu^{II}L$ complexes, the UV–visible spectra were obtained for all systems to determine the optimal wavelengths for measuring the complex absorption. All of the copper(II)–polyamino polythiaether complexes exhibit spectra with two strong absorption bands in the visible and/or near-UV region, similar to those found for the corresponding polythiaether complexes.[31] The wavelengths for these peak maxima and the molar absorptivity values are tabulated in Table IV. For all complexes included in this study, the molar absorptivity values were sufficiently large to permit direct spectral monitoring of the complex formation kinetics even at low dilution.

Complex Formation Kinetics. The kinetics for the reaction in eq 2 were studied at 25 °C in the presence of 0.10 M $NaClO_4$ for all seven systems included in this work. In each case, the reaction kinetics were fitted to the following differential expression

$$d[Cu^{II}L']/dt = k_f[Cu^{2+}][L'] - k_d[Cu^{II}L'] \quad (23)$$

where k_f and k_d represent the rate constants for complex formation and dissociation, respectively. For each system, a series of kinetic determinations were carried out at each of several pH values under conditions where $C_{Cu} \gg C_L$ to yield the pseudo-first-order rate expression

(28) Sylva, R. N.; Davidson, M. R. *J. Chem. Soc., Dalton Trans.* **1979**, 232–235.

(29) (a) Bernardo, M. M.; Schroeder, R. R.; Ochrymowycz, L. A.; Rorabacher, D. B. To be submitted for publication. (b) Bernardo, M. M. Ph.D. Dissertation, Wayne State University: Detroit, MI, 1987.

(30) The equilibrium constant for the formation of $CuLX^+$ ($K_{1X\bullet} = a_{Cu^{II}LX^+}/a_{Cu^{II}L^{2+}}a_{X^-}$), with all terms in activities, has been determined to have a value of approximately 20 M^{-1} for a series of macrocyclic tetrathiaether complexes including $Cu^{II}([14]aneS_4)$.[3,26] For the conditions used in the current study ($[ClO_4^-] \approx 0.10$ M), this would yield $\alpha_{Cu^{II}L} = 1 + K_{1X\bullet}[X^-]f_{X^-} = 3$. Since it is much more difficult to evalute $K_{1X\bullet}$ for systems involving ligands that protonate (due to the dependence of the K_H values on ionic strength), no attempt has been made to determine the actual values of $\alpha_{Cu^{II}L}$ in this work.

(31) Jones, T. E.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1975**, *97*, 7485–7486.

(32) Siegfried, L.; Kaden, T. A. *Helv. Chim. Acta* **1984**, *67*, 29–38.

(33) Hay, R. W.; Bembi, R.; Moodie, W. T.; Norman, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2131–2136.

$$d[Cu^{II}L']/dt = k_{obs}[L'] \quad (24)$$

for which the observed first-order rate constant, k_{obs}, could be obtained from the integrated form

$$\ln\left(\frac{[Cu^{II}L]_e}{[Cu^{II}L']_e - [Cu^{II}L']}\right) = \ln\left(\frac{A_e}{A_e - A_t}\right) = k_{obs}t \quad (25)$$

which can then be analyzed directly. In this expression, $[Cu^{II}L']$ represents the total concentration of the copper complex at any time (i.e., $[CuL^{2+}] + [CuLX^+]$), $[CuL']_e$ represents the *equilibrium* concentration of the copper complex, A_t and A_e are the corresponding values of the spectrophotometric absorbance due to the copper complex as measured at the peak maximum (in the range of 335–414 nm), and t is the elapsed time for each measurement of A_t.

The formation kinetics at each pH value were measured for at least five different copper concentrations, covering at least a 10-fold range in each case; the minimum Cu(II) concentration utilized was at least 10 times that of the total ligand concentration present. For each set of concentration conditions, an average of six kinetic runs was carried out with the results statistically averaged. The resulting set of k_{obs} values obtained at each specific pH was then resolved to yield the constituent k_f and k_d values by means of the linear relationship

$$k_{obs} = k_f[Cu^{2+}] + k_d \quad (26)$$

For all systems, including those conducted at the lowest pH values, linear regression analyses yielded k_d values that were not statistically different from zero. [The resolved k_f values (representing about 30 or more individual kinetic runs for each ligand at each pH value) obtained by using eq 26 for all systems at all experimental pH values studied (representing a total of more than 1500 kinetic runs) are tabulated in the supplementary material.]

Resolution of Specific Rate Constants. The range of pH values investigated was generally limited at the upper end to pH 5.50 (or, at most, pH 5.7) due to concerns regarding the possible interference caused by precipitation of $Cu(OH)_2$. A recent investigation on related systems[17] has confirmed that the aquocopper(II) ion, Cu^{2+}, is the only species that contributes significantly to the complexation kinetics at pH < 5.7. Thus, it is presumed that all variations in the observed k_f values as a function of pH may be attributed to the varying ratios of the different protonated species of the ligands studied, as represented by the overall scheme

$$Cu^{2+} + \begin{cases} L \xrightarrow{k_{Cu}^{L}} CuL' \\ L \overset{K_{H1}^{m}}{\rightleftharpoons} HL^+ \xrightarrow{k_{Cu}^{HL}} CuL' + H^+ \\ HL^+ \overset{K_{H2}^{m}}{\rightleftharpoons} H_2L^{2+} \xrightarrow{k_{Cu}^{H_2L}} CuL' + 2H^+ \\ H_2L^{2+} \overset{K_{H3}^{m}}{\rightleftharpoons} H_3L^{3+} \xrightarrow{k_{Cu}^{H_3L}} CuL' + 3H^+ \end{cases} \quad (27)$$

The triprotonated ligand species is feasible only in the case of [14]aneN$_3$S, and even this ligand showed no evidence of a significant kinetic contribution for the $k_{Cu}^{H_3L}$ term. Thus, on the basis of the foregoing scheme, the resolved k_f term from eq 23 can be rewritten as the sum of the contributions of the L, HL^+, and H_2L^{2+} species as follows:

$$k_f\alpha_L = k_{Cu}^{L} + k_{Cu}^{HL}K_{H1}^{m}a_H + k_{Cu}^{H_2L}K_{H1}^{m}K_{H2}^{m}(a_H)^2 \quad (28)$$

Of principal interest in this work was the evaluation of the specific rate constant involving the unprotonated ligand, k_{Cu}^{L}. Thus, for all systems eq 28 was initially treated in the simplified linear form:

$$k_f\alpha_L = k_{Cu}^{L} + k_{Cu}^{HL}K_{H1}^{m}a_H \quad (28')$$

Plots of $k_f\alpha_L$ vs a_H were then evaluated by linear regression analysis to yield the optimum values of the intercept (k_{Cu}^{L}) and slope ($k_{Cu}^{HL}K_{H1}^{m}$).

Table V. Summary of Specific Rate Constants for Aquocopper(II) Ion Reacting with Various Protonated Species of the Polyamino Polythiaethers in Aqueous Solution at 25 °C, μ = 0.10 M ($NaClO_4$)

ligand reacted	k_{Cu}^{L}, M^{-1} s^{-1}	k_{Cu}^{HL}, M^{-1} s^{-1}	$k_{Cu}^{H_2L}$, M^{-1} s^{-1}
	Quadridentate Macrocycles		
[14]aneS$_4$	1.3 × 10^5 [a]		
[14]aneNS$_3$	3.2 (2) × 10^6	1.4 (3) × 10^2	
[14]aneN$_2$S$_2$	1.6 (1) × 10^8	1.3 (6) × 10^3	–
[14]aneNSSN	8.2 (6) × 10^7	5 (2) × 10^3	–
[14]aneNSNS	2.0 (4) × 10^9	2.9 (7) × 10^5	–
[14]aneN$_3$S	–	3.1 (1) × 10^5	51 (13)
[14]aneN$_4$	–	[1.8 × 10^6] [b]	[0.39] [b]
		[8 × 10^6] [c]	[0.076] [c]
	Quinquedentate Macrocycles		
[15]aneS$_5$	7.5 × 10^5 [a]		
[15]aneNS$_4$	8.4 (4) × 10^6	1.4 (3) × 10^3	
[15]aneN$_2$S$_3$	8 (2) × 10^7	2.5 (1) × 10^5	≈8 (1)
[15]aneN$_5$	–	–	[9.7 × 10^4] [d]

[a] Reference 16. [b] Reference 13f (μ = 0.5 M (KNO_3); data corrected for complexation of Cu(II) ion by acetate buffer). [c] Reference 11b (μ = 0.2 M; data corrected for complexation of Cu(II) ion by acetate buffer). [d] Reference 11d (μ = 0.2 M; data corrected for complexation of Cu(II) ion by acetate buffer).

For all systems studied other than [14]aneN$_3$S (vide infra), reasonable k_{Cu}^{L} and k_{Cu}^{HL} values were obtained from these plots. However, large relative standard deviations were observed for the k_{Cu}^{L} value in the case of [15]aneN$_2$S$_3$ due to the relatively high reactivity of the monoprotonated species, which dominates the k_f term in the pH range studied. For this system, the k_{Cu}^{L} value is considered reliable only to an order of magnitude.

When plotted in the form of eq 28′, the [14]aneN$_3$S data yielded an intercept that was not statistically different from zero (i.e., the contribution of the k_{Cu}^{L} term was negligible), and the plot showed upward curvature as the activity of hydrogen ion increased, indicating that the kinetic contribution of the H_2L^{2+} species was significant in the pH range studied. Therefore, the data for this system were replotted in the form

$$k_f\alpha_{HL} = k_{Cu}^{HL} + k_{Cu}^{H_2L}K_{H2}^{m}a_H \quad (28'')$$

where

$$\alpha_{HL} = [L']/[HL^+] = \alpha_L/K_{H1}^{m}a_H \quad (29)$$

With linear regression analysis, a plot of $k_f\alpha_{HL}$ vs a_H yielded reasonable slope and intercept values, thereby permitting the evaluation of $k_{Cu}^{H_2L}$ for this system.

The choice of the borate–mannitol system, as a known noncomplexing buffer for aquocopper(II) ion,[34] tended to restrict the lower pH limit to about 4.5. Although this was generally sufficient to permit a reasonable evaluation of the k_{Cu}^{HL} value for most systems, the lack of satisfactory linearity for the [14]aneN$_2$S$_2$ system prompted us to extend the pH study for this system to lower values. The pH range was subsequently extended to pH 3.10, thereby permitting a satisfactory value of k_{Cu}^{HL} to be obtained.[35]

In the case of [14]aneNSNS and [15]aneN$_2$S$_3$, the sizeable values obtained for k_{Cu}^{HL} suggested that the $k_{Cu}^{H_2L}$ term might also be measurable. An attempt was made to obtain this specific rate constant for the latter system by measuring the reaction kinetics at pH 1.00 and 2.00 (in the absence of buffer). When eq 28″ was applied to the data obtained at these low pH values

(34) Moss, D. B.; Lin, C.-T.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1973**, *95*, 5179–5185.

(35) The addition of $HClO_4$ to solutions containing equimolar H_3BO_3 and $H_2BO_3^-$ in the presence of saturated mannitol permitted lower pH values to be attained, although the solutions were poorly buffered at the lowest end of this pH range. Subsequently, we have studied reactions at pH 3.0–4.5 by buffering with a mixture of mono- and diprotonated *N,N,N′,N′*-tetraethylmethylenediamine, a Lewis base that is known to be too sterically hindered to permit metal complexation (see ref 21).

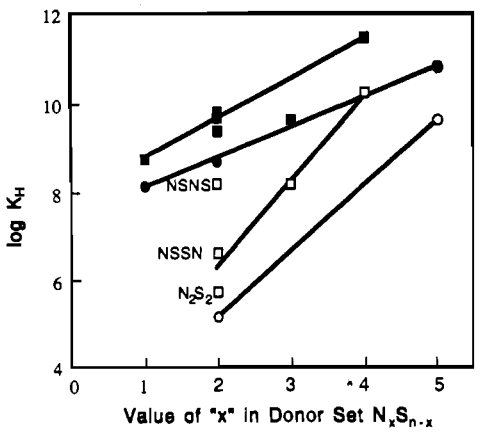

Figure 2. Plot of log $K_H{}^m$ values for the macrocyclic polyamino polythiaether ligands as a function of the number of nitrogen donor atoms (x). Symbols: for log K_{H1}, (■) [14]aneN_xS_{4-x} ligands and (●) [15]aneN_xS_{5-x} ligands; for log K_{H2}, (□) [14]aneN_xS_{4-x} ligands and (○) [15]aneN_xS_{5-x} ligands.

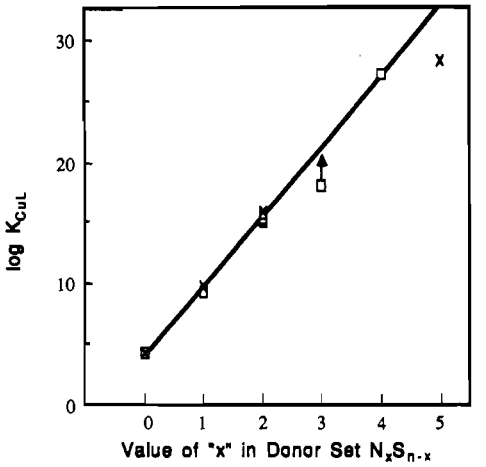

Figure 3. Plot of log $K_{CuL''}$ values for the Cu(II) macrocyclic polyamino polythiaether complexes as a function of the number of nitrogen donor atoms (x). The value for Cu^{II}([14]aneN_3S) is marked with an arrow pointing upward since the point plotted is considered a lower limit. Symbols: (□) Cu^{II}([14]aneN_xS_{4-x}) complexes; (×) Cu^{II}([15]aneN_xS_{5-x}) complexes.

(and including the data for pH 4.55–4.75, where the $k_{Cu}{}^L$ term does not make a significant contribution to the overall formation kinetics), it was found that the H_2L^{2+} species contributes only very slightly to the kinetics, even at these very acidic levels. However, these data were sufficient to permit an estimate to be made for the magnitude of $k_{Cu}{}^{H_2L}$ for the [15]aneN_2S_3 ligand.

The specific rate constants for aquocopper(II) ion reacting with the various protonated forms of all seven ligands included in this work are summarized in Table V. This table also includes the corresponding specific rate constants reported in the literature for aquocopper(II) ion reacting with the related homoleptic ligands [14]aneS_4, [15]aneS_5, and [15]aneN_5.

Discussion

Protonation Constants. Since solvation effects may have a substantial influence upon apparent donor atom basicity in aqueous solution,[36] any analysis of the protonation constant data must be undertaken with some caution. Nonetheless, the trends among similar ligands may be of some assistance in understanding ligand conformational influences and constraints.

The data in Table II reveal that, for each of the mixed-donor ligands included in this work, the first protonation constant is in the normal range found for similar open-chain polyamine and polyamino polythiaether ligands ($8 < \log K_{H1} < 10$).[37] This behavior is in contrast to the extremely large value ($\log K_{H1} \geq 11.5$) reported for the corresponding 14-membered macrocyclic tetraamine [14]aneN_4 (cyclam). The apparently anomalous protonation behavior of [14]aneN_4 led Bosnich, Poon, and Tobe to propose that the first two protons might form hydrogen bonds between two opposite (or "trans") nitrogen donor atoms (presumably involving a bridging water molecule), resulting in a puckered-ring conformation.[38] If this proposal has merit, one might expect a similarly large log K_{H1} value for [14]aneN_3S and [14]aneNSNS, since each of the latter ligands has the possibility of forming one internal trans hydrogen bond. However, both of the latter ligands have log K_{H1} values that are far smaller than the value reported for [14]aneN_4. Moreover, in the crystal structure for the perchlorate salt of H_2([14]aneN_4)$^{2+}$ (where no bridging water molecules are available), there is an indication that hydrogen bonding occurs between the protonated nitrogen donor atom and the nitrogen to which it is linked via a propylene bridge (with an N–H distance of 2.06 Å).[39] This suggests that log K_{H1} should be larger for [14]aneNSSN than for [14]aneN_2S_2, which is also not observed. In fact, all three ligands containing the N_2S_2 donor set exhibit essentially the same value of K_{H1}, suggesting that the magnitude of K_{H1} cannot easily be attributed to a specific type of internal hydrogen bond within the macrocyclic ligand.

It is interesting to note that a plot of log K_{H1} vs "x" for 14-membered cyclic ligands having the N_xS_{4-x} donor set (Figure 2) can be construed to be nearly linear, with the exception that [14]aneN_3S is out of line. The more limited data for the log K_{H1} values of the 15-membered cyclic ligands with the N_xS_{5-x} donor also appear to be linear with a similar slope. Similar linear trends are observed for the log K_{H2} values (although the values for the 14-membered N_2S_2 ligands are scattered) with a somewhat steeper slope.

Since solvent interactions are known to play a large role in the trends observed for amine nitrogen protonation constants in solution,[21,37] the regular trends in the log K_H values may be attributable to a general transition in the preferred conformations for the uncomplexed ligands from an all-*exo* conformation for [14]aneS_4 to an all-*endo* conformation for [14]aneN_4. At the very least, the smoothness of the observed trends suggests that the [14]aneN_4 protonation constants are perhaps not as anomalous as they appear at first glance. The tendency toward lower K_H values observed for the 15-membered cyclic ligands relative to their 14-membered counterparts also supports the suggestion that conformational/solvational effects play a significant role in influencing ligand protonation.

In contrast to the similarity in their K_{H1} values, the three 14-membered N_2S_2 ligands exhibit dramatically different K_{H2} values. Although this trend parallels the distance between the two nitrogen donor atoms, the 300-fold range in the K_{H2} values for these three compounds is much too large to be attributed to electrostatic factors alone. It is interesting to note, however, that the K_{H2} values for [14]aneN_3S and [14]aneNSNS, where the two protonated nitrogens are presumably in trans positions, are nearly equal, as are the corresponding values for [15]aneN_2S_3 and [14]aneN_2S_2, where the protonated nitrogens are separated by ethylene linkages. Thus, the relative positions of the nitrogen donor atoms significantly affect the magnitude of K_{H2} whatever specific factors are involved.

Stability Constants. A particularly striking observation is that the stability constants for the copper(II) complexes formed with the cyclic polyamino polythiaethers are very regular in their behavior, showing an increase of 5–6 orders of magnitude with each additional substitution of a nitrogen for a sulfur donor atom (Figure 3). This regularity is apparent even for the three 14-membered diaza dithiaether complexes, which exhibit nearly identical $K_{Cu^{II}L''}$ values despite the large differences in their kinetic behavior (vide infra). Perhaps even more surprising, the $K_{Cu^{II}L''}$

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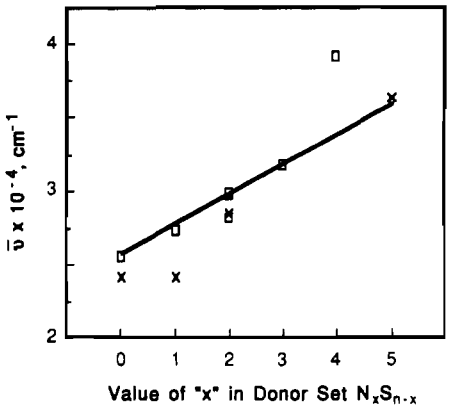

Figure 4. Plot of the relative energies of the higher energy absorption peak observed in the UV–visible spectra of the Cu(II) polyamino polythiaether complexes as a function of the number of nitrogen donor atoms (x). (□) $Cu^{II}([14]aneN_xS_{4-x})$ complexes; (×) $Cu^{II}([15]aneN_xS_{5-x})$ complexes.

values for the $[14]aneN_xS_{4-x}$ and $[15]aneN_xS_{5-x}$ series of complexes are nearly identical for ligands having the same value of x. Within these series of ligands, it appears that the dominant factor contributing to the stability constants is simply the intrinsic basicity of the donor atoms.

As illustrated in Figure 3, only two complexes deviate from the general trend, and one of these is the $Cu^{II}([14]aneN_3S)$ complex for which the reported $K_{Cu^{II}L''}$ value is merely a lower limit. The trend established by the other ligand systems suggests, in fact, that the log $K_{Cu^{II}L''}$ value for the $[14]aneN_3S$ complex should be ≈20. (The other deviant system is $Cu^{II}([15]aneN_5)$ in which, by analogy to $[15]aneS_5$,[40] the fifth nitrogen donor must occupy an axial position where it cannot bond as effectively.) Since the $[14]aneN_4$ ligand (cyclam) and its substituted derivatives have been the subject of several fundamental studies on the "macrocyclic effect",[2,5,41] it is particularly reassuring to note that the latter ligand is consistent with the systematic increase in stability constants within this series of macrocyclic ligand complexes.

Spectral Characteristics. From the data in Table IV, it is evident that the UV and visible absorption peaks for the copper(II)–polyamino polythiaether complexes shift to higher energies as the number of nitrogen donor atoms increases. In fact, as illustrated in Figure 4 for the higher energy peak, the relationship between the wavenumbers of the peak maxima and the value of x in the case of the $Cu^{II}([14]aneN_xS_{4-x})$ complexes is essentially linear. The major exception to this trend is the $Cu^{II}([14]aneN_4)$ complex for which a much higher energy band is observed. These observations would appear to be consistent with the assignment of this peak to a S → Cu(II) charge-transfer band[42] such that, as the number of sulfur donor atoms increases, the energy of the electronic transition decreases.

Interestingly, the various arrangements of donor atoms in the three diaza dithiaether ligands cause only small perturbations in the peak maxima. This suggests that the orbital overlap is little affected by the specific arrangement of the donor atoms. For the quinquedentate ligands, the energies of the peak maxima appear to be slightly lower than those exhibited for the quadridentate ligands, although the more limited data prevent the formulation of any general conclusions.

General Mechanistic Considerations. The general mechanism for an aquometal ion reacting with a simple unidentate ligand is understood in considerable detail.[43] For Cu(II), as with most

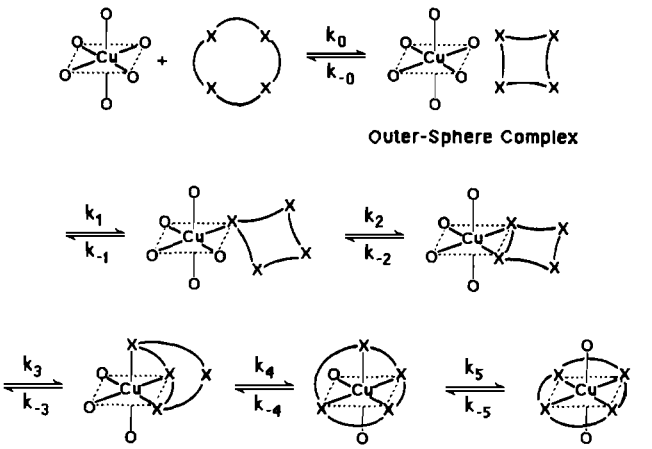

Figure 5. Schematic mechanism for the stepwise complexation of a quadridentate macrocyclic ligand with $Cu(H_2O)_6^{2+}$ (hydrogen atoms on the coordinated water molecules and the nitrogen donor atoms omitted). The first three donor atoms are required to coordinate in a cofacial arrangement such that the fourth bond formation step (k_4) results in a folded complex. This is then followed by an internal rearrangement of the inner coordination sphere (step k_5). An essentially identical mechanism is presumed to occur for the quinquedentate ligands with the exception that the step labeled k_5 involves the coordination of the fifth donor atom and the corresponding loss of the remaining inner-sphere water molecule.

of the later transition-metal ions, the process is primarily dissociative (or dissociative interchange, I_d)[43,44] in which the leaving innersphere water molecules are little influenced by the nucleophilicity of the incoming donor atom(s). The reaction of a single unidentate ligand with aquocopper(II) ion may be represented by a two-step process (the Eigen mechanism) as follows:[43]

$$Cu(H_2O)_6^{2+} + L \overset{K_{os}}{\rightleftharpoons} \underset{\text{outer-sphere complex}}{Cu(H_2O)_6^{2+}\cdot L} \overset{k^{Cu-H_2O}}{\rightleftharpoons} CuL(H_2O)_5^{2+} + H_2O \quad (30)$$

In this scheme, K_{os} represents the equilibrium constant for the formation of an outer-sphere complex (i.e., an outer-sphere contact pair, $Cu(aq)^{2+}\cdot L$) and k^{Cu-H_2O} represents the rate constant for the rupture of an inner-sphere metal–water bond, which is accompanied by rapid insertion of a ligand donor atom.

Assuming a steady-state concentration of the outer-sphere complex, the resolved rate constant for aquocopper(II) ion reacting with a simple ligand should yield the relationship[43]

$$k_{Cu}{}^{L} = K_{os}k^{Cu-H_2O} \quad (31)$$

For an open-chain multidentate ligand, the overall mechanism of complex formation may be represented as a series of steps in which the rupture of a metal–water bond is quickly followed by the insertion of a donor atom from the attacking ligand at the site being vacated. For strongly coordinating multidentate ligands, this process continues until all donor atoms have formed bonds with the central metal ion (or until all sites on the central metal ion are occupied by ligand donor atoms).

In the case of those macrocyclic ligands that coordinate in a planar array, the reduced flexibility of the ligand imposes additional constraints upon the complexation process in that the first three coordinate bonds must initially occupy sites that are cofacial. The proposed mechanism for a representative macrocyclic quadridentate ligand reacting with aquocopper(II) ion is represented schematically in Figure 5.[15]

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As with other multidentate ligand systems, it is presumed that the rate-determining step in the formation of metal complexes with macrocyclic ligands will not occur beyond the point of the second coordinate bond formation (i.e., the closure of the first chelate ring, designated by the stepwise rate constant k_2 in Figure 5).[45] Thus, the bonding of the third donor atom at a cofacial site should not enter into the observed formation rate constants but should be manifested solely in the dissociation rate constants. Nonetheless, in analyzing the general mechanistic details outlined in Figure 5, the reactivity of a macrocyclic ligand may be considerably more subject to ligand conformational effects than is the case with corresponding open-chain ligands.

The initial accessibility of an individual donor atom to an inner-sphere site on the metal ion requires that the cyclic ligand be in an exo conformation[14] (or at least be exo in the vicinity of the donor atom involved in first coordinate bond formation) so that the available unshared pair of electrons on the donor atom in question is directed toward the ligand periphery and away from the ligand cavity.[15] For the formation of the second and subsequent bonds, the ligand must undergo a series of concerted internal bond rotations in order to bring a second proximal donor atom into position for bonding at a cis inner-sphere site. Since the macrocyclic ligands contain no floppy "ends", the constraints upon the formation of the initial exo conformation and upon the internal ligand bond rotations for subsequent bonding steps are much more likely to be restricted and, therefore, much more easily influenced by subtle changes in the ligand structure, as well as by the ligand solvation. (These conformational effects are particularly apparent in macrocyclic ligands that have substituents on the ligand backbone.)[15,17]

Formation Rate Constants for the Aquocopper(II) Ion Reacting with the Polyamino Polythiaether Ligands. The data in Table V reveal that there is a general tendency for the formation rate constants to increase as the number of nitrogen donor atoms in the macrocycle increases. In fact, a plot of log $k_{Cu}^{H_nL}$ vs the number of nitrogen donor atoms is found to be relatively linear for each specific rate constant type (k_{Cu}^{L}, k_{Cu}^{HL}). However, as suggested by the notable differences in the values obtained for the three ligands containing two sulfurs and two nitrogens, the relationship is not a simplistic one and several phenomena are believed to influence these values. The contributing factors are discussed below.

Kinetic Comparisons for Unprotonated Ligand Species. The simplest substitution reaction previously studied for aquocopper(II) ion is that involving ammonia as the incoming ligand. The formation rate constant for this reaction, as measured in aqueous solution ($k_{Cu}^{NH_3} = 2 \times 10^8$ M^{-1} s^{-1}),[46,47] has been shown to be in excellent agreement with the theoretical value based upon the Eigen dissociative mechanism (eq 31), viz., at 25 °C

$$k_{Cu}^{NH_3} = K_{os}k^{Cu\text{-}H_2O}(cf) = (0.1\ M^{-1})(2.8 \times 10^9\ s^{-1})(3/4) \quad (31')$$

$$k_{Cu}^{NH_3} \approx 2 \times 10^8\ M^{-1}\ s^{-1}$$

where the value of K_{os} is calculated assuming the absence of steric factors and the value of $k^{Cu\text{-}H_2O}$ is obtained from a reinterpretation of Merideth and Connick's NMR relaxation measurements involving inner-sphere water exchange on $Cu(H_2O)_6^{2+}$.[47] The "competition factor", cf = $^3/_4$, which is often omitted, represents the statistical correction for a ligand donor atom in the outer-sphere competing with outer-sphere water molecules for a vacant inner-sphere site.[48]

From previous kinetic studies on complex formation involving aquonickel(II) ion, it has been estimated that the steric hindrance induced by the substitution of two alkyl chains (of two carbon atoms each or longer) on a donor atom should diminish the formation rate constant with that donor atom by a factor of 50–250.[21,49] Treating each donor atom in the macrocycle as a separate entity with an alkyl "tail" introduces a factor of 4 to account for the four donor atoms and yields the following theoretical estimate for the rate constant for the *first* bond formation of aquocopper(II) ion reacting with a neutral quadridentate ligand:[50]

$$k_{Cu}^{L} \cong 4k_{Cu}^{NH_3}/(50\text{–}250) \approx (3 - 16) \times 10^6\ M^{-1}\ s^{-1} \quad (32)$$

This approach presumes that there are no additional steric effects associated with the cyclization of the ligand other than those imposed by the alkyl substituents on the donor atoms.

In previously analyzing the formation rate constants for aquocopper(II) ion reacting with several cyclic polythiaethers,[16] it was noted that the observed formation rate constant for the reaction with [14]aneS$_4$ (see Table V) is more than 1 order of magnitude smaller than the value predicted by eq 32. This was interpreted as an indication that the rate-determining step might be at the point of second bond formation (i.e., chelate ring closure). This presumed shift in the position of the rate-determining step was attributed to the weak donating ability of thiaether sulfur atoms with Cu(II), resulting in the situation where $k_{-1} \gg k_2$ (Figure 5). Alternatively, however, it was noted that the difference between the experimental and theoretical formation rate constant values could be attributable to ligand conformational effects that might reduce the fraction of ligand in the reactive exo conformation, thereby resulting in an apparent increase in the extent of steric hindrance.

The polyamino polythiaether ligands were specifically selected for the current study to reduce this ambiguity. By providing one or more strongly bonding amine nitrogen donor atoms, the rate-determining step should be at the point of first bond formation whenever a Cu–N bond forms initially. On the basis of this hypothesis, the presence of a single nitrogen donor atom in the [14]aneNS$_3$ ligand suggests that the theoretical formation rate constant with the unprotonated species should be on the order of (0.75–4) $\times 10^6$ M^{-1} s^{-1} (i.e., one-fourth the value predicted in eq 32 for a system involving four strongly bonding donor atoms). This prediction is based on the assumption that the first bond formation (with the nitrogen donor atom) is rate determining and that there are no additional steric effects associated with the macrocyclic ligand relative to open-chain ligands. The value of $k_{Cu}^{L} = 3.2 \times 10^6$ M^{-1} s^{-1} for [14]aneNS$_3$ obtained in this study (Table V) is exactly within this range—indicating that *conformational effects have little influence upon the first bond formation process for this macrocycle.*

The preceding discussion may be overly simplified, as suggested by the fact that the k_{Cu}^{L} value for [15]aneNS$_4$ is 8.4 $\times 10^6$ M^{-1} s^{-1}, or about 2$^1/_2$-fold larger than the corresponding value for [14]aneNS$_3$. Also, the k_{Cu}^{L} value for [15]aneS$_5$ is about 6-fold larger than the corresponding value for [14]aneS$_4$, suggesting that the larger ligands are more flexible and that ligand conformation does, in fact, play a small role in influencing the rate of metal complex formation in the 14-membered macrocyclic ligands. In fact, the observation that the experimental value of k_{Cu}^{L} for [15]aneNS$_4$ exceeds the theoretical value predicted in the preceding paragraph implies that steric effects are smaller for bonding to the nitrogen donor atom in this macrocycle than for a simple R$_2$NH open-chain ligand. This implies that, *in the prevailing macrocyclic conformation, the two ethylene chains tend to be*

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(48) The factof of $^3/_4$ derives from the assumption that eight species in the outersphere (centered over the eight octahedral faces) compete for six innersphere sites: Neely, J.; Connick, R. *J. Am. Chem. Soc.* **1970**, *92*, 3476–3478.
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(50) See discussion in ref 16, p 3518, and references therein.

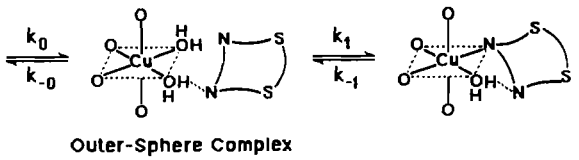

Figure 6. Schematic representation of the internal conjugate base (ICB) mechanism in the early steps of complex formation with a macrocyclic ligand, showing the formation of a hydrogen bond between a strongly basic (i.e., nitrogen) donor atom and a coordinated water molecule in the outer-sphere complex (hydrogen atoms shown only for the two coordinated water molecules involved). This hydrogen bond decreases the value of k_{-1} and, therefore, increases the relative concentration of the outer-sphere complex species. The hydrogen bond must remain intact at the point of the rate-determining step (i.e., for the case shown, at the point of first donor atom insertion represented by the stepwise rate constant k_1), suggesting that the distance between the two nitrogen donor atoms and their relative orientations should be important factors. (See Figure 5 for comparison.)

folded away from the available lone pair on the nitrogen.

An examination of the kinetic data in Table V reveals that the k_{Cu}^{L} values for the various diamine macrocycles, [14]aneN_2S_2, [14]aneNSNS, [14]aneNSSN, and [15]aneN_2S_3, are 1–3 orders of magnitude larger than are the values for the corresponding monoamine macrocycles. This behavior is consistent with previous studies on open-chain diamines in which the latter compounds have been observed to react much more rapidly than ammonia (and other monoamines). For example, in the case of aquonickel(II) ion, the observed increase in the complex formation rate constant with ethylenediamine (en) compared to ammonia, after correcting for steric and statistical effects, amounts to 200-fold:[20b]

$$(k_{Ni}^{en}/k_{Ni}^{NH_3})(\rho/2) = (3.4 \times 10^5)/(4.6 \times 10^3)(5/2) \approx 200 \quad (33)$$

(The factor of $^5/_2$ corrects for an anticipated 5-fold steric factor (ρ) in the case of ethylenediamine and a 2-fold statistical correction to account for the presence of two nitrogens in ethylenediamine.) For aquocopper(II) ion, a similar enhancement occurs, although the observed increase is only 50-fold:[34]

$$(k_{Cu}^{en}/k_{Cu}^{NH_3})(\rho/2) = (4 \times 10^9)/(2 \times 10^8)(5/2) = 50 \quad (34)$$

However, this latter increase is artificially limited by the fact that the reaction involving ethylenediamine appears to have reached the diffusion limit.[34]

The general rate constant enhancement observed with ethylenediamine and related ligands has been attributed to hydrogen bond formation in the outer-sphere complex between a coordinated water molecule and a basic nitrogen donor atom of the ligand (the so-called *internal conjugate base* (ICB) mechanism),[20] resulting in an increase in the magnitude of the K_{os} value. In order to promote complex formation, this hydrogen bond must still be intact at the time of the rate-determining step, implying that it will only be a significant factor when a second strongly bonding donor atom on the attacking ligand is present in a proximal position favorable for first coordinate bond formation (Figure 6).

In the case of the macrocyclic polyamino polythiaether ligands, the ICB effect might be expected to result in observed rate constants for the diamines that are as much as 400 times larger (200 × 2) than the corresponding monoamine values, since the ostensible steric effects (corresponding to the factor of 5 in eqs 33 and 34) should be essentially the same for both macrocyclic species while the 2-fold statistical factor, favoring the diamine over the monoamine, remains. (This ignores the differences in the intrinsic basicities of the ethylenediamine nitrogens relative to the macrocyclic diamines, a factor that would be expected to influence the strength of the outer-sphere hydrogen bond[21] and, therefore, the magnitude of the K_{os} enhancement.) The observed rate constant enhancements for [14]aneN_2S_2, [14]aneNSSN, and [14]aneNSNS relative to [14]aneNS_3 are approximately 50, 30, and 600, respectively, while for [15]aneN_2S_3 the enhancement relative to [15]aneNS_4 is 10-fold. For the most part, the differences in these observed enhancements presumably reflect both the uncertainties in the experimental data and the differences in the preferred conformations of these macrocyclic ligands. The fact that only [14]aneNSNS exhibits an enhancement in the range of the predicted theoretical value is surprising since the arrangement of the two nitrogens on opposite sides of the ring might be expected to reduce or eliminate the ability of one nitrogen donor atom to form a hydrogen bond to the aquocopper(II) ion at the same time that the second nitrogen is undergoing substitution into the inner coordination sphere. Molecular models do indicate that a syn conformation can readily exist for this ligand in which favorable outer-sphere hydrogen bonding may be achieved, but entropy considerations would make it appear that this ligand would be the least likely to exhibit a sizeable ICB effect. Molecular mechanics calculations would be useful in exploring this situation more extensively.

Kinetic Comparisons for Protonated Ligand Species. For the macrocyclic polyamine and polyamino polythiaether ligands, protonation of the ligand is presumed to influence the reaction kinetics in four ways: (i) internal hydrogen bonding may constrain the ability of a ligand to adopt an exo conformation; (ii) interactions of the protonated sites with the solvent may alter the relative stability of the preferred ligand conformations; (iii) the electrostatic repulsive forces between the protonated site and the positively charged metal ion may be enhanced relative to similar open-chain ligands since the maximum distance of the attacking metal ion from the protonated site is much more limited for cyclic species; and, (iv) in the case of the fully protonated polyamino polythiaethers, only the weakly bonding sulfur donor atoms would be available for bond formation in the early steps of complexation. By correlation to the proposed mechanism for macrocyclic polythiaethers, this last effect could shift the position of the rate-determining step to the point of chelate ring closure (i.e., the step represented by rate constant k_2 in Figure 5).

In considering the formation rate constants for the monoprotonated ligands, electrostatic repulsion between the metal ion and the protonated donor atom site should influence the ability of the metal ion to approach closely to the remaining donor atoms in the outer-sphere complex. In fact, this repulsion might be expected to favor initial bond formation at a site distal from the point of protonation, i.e., involving the donor atom on the opposite side of the macrocyclic cavity. However, depending upon the actual ligand conformations, model calculations suggest that the effect of electrostatic repulsion may alter the k_{Cu}^{HL} value by no more than a factor of 3, even if the first bond formation occurs at a site proximal to the protonated nitrogen donor.[51]

For [14]aneNS_3, the observed k_{Cu}^{L}/k_{Cu}^{HL} ratio is approximately 2×10^4. This huge difference clearly cannot be attributed to electrostatics. The only available donor atoms in the H([14]aneNS_3)$^+$ species are sulfur donor atoms, which, on the basis of our earlier analysis of the polythiaether kinetics, suggests that the rate-determining step for the reaction of Cu^{2+} with HL^+ should be at the point of second bond formation (i.e., chelate ring closure) for this system. However, the ratio of k_{Cu}^{L} for [14]aneS_4 to k_{Cu}^{HL} for H([14]aneNS_3)$^+$ is still 1×10^3. Thus, the k_{Cu}^{HL} value involving H([14]aneNS_3)$^+$ must be considered to be anomalously small. The most logical explanation for this discrepancy is that the protonation of [14]aneNS_3 greatly alters the conformational equilibria of this ligand in favor of unreactive conformers.

In extending the foregoing line of reasoning, chelate ring closure with H([14]aneNS_3)$^+$ requires that one of the sulfur donor atoms involved in closing the first chelate ring must be adjacent to the protonated nitrogen; the electrostatic contribution for this reaction would be expected to be greater than for H([15]aneNS_4)$^+$. In the latter case, chelate ring closure does not require the involvement of a proximal sulfur atom. Thus, for the latter 15-membered macrocycle, the k_{Cu}^{L}/k_{Cu}^{HL} ratio is 6×10^3 while the ratio of k_{Cu}^{L} for [15]aneS_5 to k_{Cu}^{HL} for H([15]aneNS_4)$^+$ is 5×10^2—each ratio being about one-fourth that observed for the 14-membered ring system. Nonetheless, the k_{Cu}^{HL} values for both H([14]aneNS_3)$^+$ and H([15]aneNS_4)$^+$ must be regarded as un-

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usually small. We conclude that *the influence of solvation on the ligand conformational equilibria is consistently different for protonated cyclic ligands than for their corresponding unprotonated species.*

Monoprotonated diamine ligands still retain an unprotonated nitrogen donor atom that is available for first bond formation. However, since only one nitrogen donor atom is available, the ICB effect is no longer operable for these HL^+ species. A comparison of k_{Cu}^{L} for [14]aneNS$_3$ with k_{Cu}^{HL} for H([14]aneN$_2$S$_2$)$^+$, H([14]aneNSSN)$^+$, and H([14]aneNSNS)$^+$ yields ratios of 2×10^3, 6×10^2, and 10, respectively. The trend in these ratios is in the same order as the increasing distance between the two nitrogen donor atoms, but all three ratios are *very much* larger than might be anticipated on the basis of electrostatic factors alone. These large kinetic effects suggest that the monoprotonated ligands have conformations that inhibit first bond formation to the Cu^{2+} ion; in fact, it is particularly noteworthy that the k_{Cu}^{HL} values for the diaza dithiaether ligands exactly parallel the K_{H2} values, which might be anticipated if internal hydrogen bonding of the first proton on the ligand were influencing both phenomena. For the 15-membered macrocycles, the ratio of k_{Cu}^{L} for [15]aneNS$_4$ to k_{Cu}^{HL} for H([15]aneN$_2$S$_3$)$^+$ is 30, a ratio which still is 10-fold larger than could be attributable to electrostatic factors. The comparative kinetic behavior of H([14]aneN$_2$S$_2$)$^+$ and H([15]aneN$_2$S$_3$)$^+$ again implies that *the 15-membered macrocyclic ligands are more flexible and less susceptible to conformational influences.*

In the case of the monoprotonated species of [14]aneN$_3$S, two unprotonated nitrogen donor atoms are still available, implying that an accelerative ICB effect could still be effective with this species. However, the observed k_{Cu}^{HL} value for H([14]aneN$_3$S)$^+$ is similar to the corresponding rate constant for H([14]aneNSNS)$^+$. Thus, any accelerative effect is masked by a counterbalancing conformational effect.

For both [14]aneN$_3$S and [15]aneN$_2$S$_3$, specific rate constant values for the diprotonated species have also been estimated. Even though a third nitrogen is available for first bond formation in the case of the former ligand, the observed $k_{Cu}^{H_2L}$ value is nearly 5 orders of magnitude smaller than k_{Cu}^{L} for [14]aneNS$_3$. This very large decrease is presumed to represent a combination of electrostatic and conformational effects. For H$_2$([15]aneN$_2$S$_3$)$^{2+}$, only sulfur donor atoms are available for initial coordinate bonding, which should shift the rate-determining step back to the point of second bond formation. As a result, the kinetic considerations for this ligand should parallel those for H([14]aneNS$_3$)$^+$ with a somewhat larger electrostatic effect and conformational differences. Again, it is apparent that conformational effects dominate the reactivity of these ligands.

Additional Observations. Of the complexes included in this study, all dissociate rapidly in strongly acidic media ($\geq$1.0 M H^+) with the exception of the Cu([14]aneN$_2$S$_2$)$^{2+}$ complex. Depending upon the specific hydrogen ion activity, this complex requires several weeks for dissociation to occur. Similarly, in the range of pH 1–2, this complex is extremely sluggish to form, as has been previously noted by Kaden, Zuberbühler, and co-workers.[19] This behavior is in dramatic contrast to the kinetic behavior of Cu([14]aneNSSN)$^{2+}$ and Cu([14]aneNSNS)$^{2+}$ under similar conditions, suggesting that [14]aneN$_2$S$_2$ must exhibit some unique features.

Our proposed explanation for this phenomenon is based on a consideration of the crystal structures previously obtained for the Cu(II) complexes formed with [14]aneS$_4$ and related macrocycles[40,52] in which it has been observed that all four donor atoms are coplanar with the Cu(II) atom; but the donor atoms bridged by ethylene groups are coordinated in an anti configuration, whereas those bridged by propylene groups are coordinated in a syn configuration (Figure 7). An analysis of the step-by-step dissociation pathway for Cu([14]aneN$_2$S$_2$)$^{2+}$ indicates that one of the two nitrogens must invert before complete dissociation is

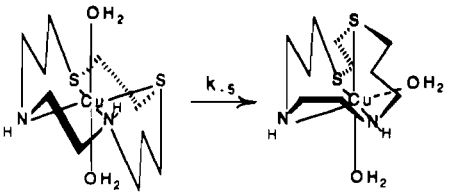

Figure 7. Schematic representation of the first step in the dissociation of the Cu^{II}([14]aneN$_2$S$_2$) complex (see Figure 5), illustrating the possible inversion of one of the coordinated nitrogen donor atoms (on the right) during the conversion of the coordinated macrocyclic ligand from a planar to a folded conformation. This inversion process (which could occur at some other step in the dissociation process) is proposed to account for the extremely sluggish dissociation kinetics observed for this complex in highly acidic solutions (see text).

effected. This inversion may occur in the conversion of the planar complex to a folded conformation (Figure 7; cf., Figure 5) or at some later stage. Such an inversion is facilitated by the momentary abstraction of the hydrogen from the nitrogen to be inverted (to form a temporary imide), a process which becomes extremely unfavorable in highly acidic solutions. The specific details for the complex formation phenomenon involving H$_2$([14]aneN$_2$S$_2$)$^{2+}$ have not been analyzed in detail, but it is noted that the energy barrier for internal rotation of the ethylene bridge would appear to be increased by the necessity for eclipsing the hydrogens on the two protonated nitrogens, a factor that could affect more than one step in the complexation process.

Whatever the source of the sluggish kinetics for the [14]aneN$_2$S$_2$ system in strongly acidic media, the observed behavior is sufficiently unique to serve as a benchmark for this ligand. It is to be expected that this unusual phenomenon may give rise to specific applications for this system under very acidic conditions.

Conclusions. The major conclusions derived from studies on the [14]aneN$_x$S$_{4-x}$ and [15]aneN$_x$S$_{5-x}$ ligands and their copper(II) complexes may be summarized as follows:

1. The linear increase in the value of log K_{H1} as x increases is attributed to a regular progression in the macrocyclic ligand conformation from an all-*exo* conformation for [14]aneS$_4$ to an all-*endo* conformation for [14]aneN$_4$.

2. The value of $K_{Cu^{II}L}$ increases by 5–6 orders of magnitude for each replacement of a thiaether sulfur donor atom by an amine nitrogen donor atom.

3. The energy of the major absorption peak (in the vicinity of 300–400 nm) for the Cu^{II}([14]aneN$_x$S$_{4-x}$) complexes shows a linear dependency on the number of sulfur donor atoms; this is consistent with the previous assignment of this peak to a S $\rightarrow$ Cu(II) charge-transfer band.

4. The formation rate constant values for the reaction of aquocopper(II) ion with *unprotonated* [14]aneNS$_3$ and [15]aneNS$_4$ (k_{Cu}^{L}) are consistent with theoretically predicted values based on simple secondary amines such as Et$_2$NH; this implies that the first bond formation with the lone nitrogen donor atom is the rate-determining step with no kinetic effects arising from ligand cyclization. The corresponding rate constant values for the *monoprotonated* ligand species of these same ligands (k_{Cu}^{HL}) are about 3 orders of magnitude smaller than their analogues containing all thiaether sulfur donor atoms, suggesting that H([14]aneNS$_3$)$^+$ and H([15]aneNS$_4$)$^+$ are significantly influenced by conformational effects.

5. The Cu^{II}L formation rate constant values for *unprotonated* diaza dithiaether macrocycles show strong evidence for an accelerative ICB mechanism. The corresponding values for *monoprotonated* diaza dithiaethers are generally much smaller than can be ascribed to electrostatic effects and imply a significant shift to less reactive conformers with increasing protonation (perhaps attributable to internal hydrogen bonding). These results suggest that the conclusions reached by previous investigators in obtaining resolved complex formation rate constants for *only* the mono- and diprotonated species of the macrocyclic polyamine ligands *are prone to erroneous interpretation in terms of the influence of ligand cyclization upon kinetic behavior.*

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6. Both the formation and dissociation kinetics of the Cu^{II}([14]aneN$_2$S$_2$) complex are found to be extremely sluggish in strongly acidic solution where the terms involving two hydrogen ions are presumed to predominate. This phenomenon is attributed to the difficulty in inverting a coordinated nitrogen during the stepwise bonding and dissociation process and should influence all similar macrocyclic ligands involving two nitrogens separated by an ethylene linkage.

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Registry No. [14]aneN$_2$S$_2$, 87939-30-8; [14]aneNSSN, 87939-29-5; [14]aneNS$_3$, 87939-28-4; [14]aneNSNS, 55702-76-6; [15]aneNS$_4$, 116319-25-6; [15]aneN$_2$S$_3$, 78988-82-6; [14]aneN$_3$S, 87939-31-9; Cu, 7440-50-8.

Supplementary Material Available: Seven tables containing resolved formation rate constant (k_f) values as a function of pH for the seven systems studied and text describing additional information about the tables (5 pages). Ordering information is given on any current masthead page.

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Evaluation of the π-Bonding Ability of Imidazole: Structure Determination and Characterization of *catena*-$(H_2O)_2(1\text{-}CH_3im)_2Mg(\mu\text{-}CN)(CN)_4(1\text{-}CH_3im)Fe^{III}\cdot H_2O$ ($1\text{-}CH_3im$ = 1-Methylimidazole)[1]

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The preparation of *catena*-diaquabis(1-methylimidazole)magnesium(II)-μ-cyanotetracyano(1-methylimidazole)ferrate(III) monohydrate (**3**) is reported. Crystals of *catena*-[Mg(H$_2$O)$_2$(1-CH$_3$im)$_2$(μ-CN)Fe(CN)$_4$(1-CH$_3$im)]·H$_2$O (1-CH$_3$im = 1-methylimidazole) are monoclinic, space group $P2_1$, with a = 8.471 (2) Å, b = 15.678 (4) Å, c = 9.722 (2) Å, V = 1190.5 (4) Å^3, Z = 2, and R (R_w) = 0.026 (0.029) for 2104 reflections. The structure contains (CN)$_5$Fe(1-CH$_3$im)$^{2-}$ units linked in extended chains through bridging cyanides (cis to 1-CH$_3$im), which are coordinated to the Mg^{2+} counterions. Two N(CN$^-$), two O(H$_2$O), and two N(1-CH$_3$im) coordinate to Mg. The chains are bent about the N of the bridging cyanides at angles of 156.3 (2) and 152.3 (3)°. The bending is attributed to a combination of electronic effects due to back-bonding, electrostatic attraction between the metal centers, and hydrogen bonding. The Fe–N(1-CH$_3$im) bond length [1.950 (2) Å] is shorter than the Fe–NH$_3$ bond lengths of similar complexes. The imidazole ring coordinated to Fe is staggered with respect to the cis cyanides, but at an angle (ϕ = 34.5°) that is less than the sterically favorable 43.6°. The cyanide trans to the 1-CH$_3$im ligand on the Fe has a shorter bond length [1.130 (4) Å] than the average cis cyanide bond length of 1.146 Å. The N$_3$–C$_2$ bond length is longer for the 1-CH$_3$im coordinated to Fe than for those of 1-CH$_3$im coordinated to Mg. The complex has a very large quadrupole splitting (from Mössbauer spectroscopy) of 2.62 ± 0.2 mm/s at 291 K (2.78 mm/s at 77 K). Collectively, our results indicate π bonding between the 1-CH$_3$im and the low-spin d^5 Fe(III). 1-CH$_3$im acts as a π *director* to align the electron hole in the dπ Fe orbitals along the Fe–N(1-CH$_3$im) axis. The electron hole primarily occupies a single orbital. The observed π-bonding properties of imidazole have important biological implications.

Introduction

The imidazole (imH, **1**) ring, a five-member nitrogen heterocycle, is an essential component of many biological systems where it occurs in proteins as part of the side chain of the amino acid histidine,[2] in nucleic acid structures as part of the purine ring of adenine and guanine,[3] and in the vitamin B_{12} coenzyme as benzimidazole.[4] In these systems the imidazole functions in a variety of roles; for example, as a proton donor and/or acceptor site for hydrogen bonding, as a specific/general base or nucleophilic catalyst, or as a site for metal ion coordination.[5-9] The imidazole moiety of histidyl residues in a large number of metalloproteins constitutes all or part of the binding sites for various transition-metal ions such as Mn^{2+}, $Fe^{2+,3+}$, $Cu^{+,2+}$, and Zn^{2+}.[8-10] Thus, structural and spectroscopic studies that characterize the bonding between imidazole and transition-metal ions are of considerable importance. Particular attention has been paid to studies of the Fe–imidazole bond because of the role of this bond in the O_2 binding cooperativity mechanism of hemoglobin[11] and in influencing the oxidation–reduction potentials of c-type cytochromes.[12] One approach to the study of Fe–imidazole bonding has been to employ smaller model complexes[9] including a variety of porphyrin complexes[12b] such as the "picket fence" and "pocket" porphyrins[13] among others. An even simpler series of complexes that have also proven useful for evaluating imidazole bonding are complexes of the type $(CN)_5FeL^{3-,2-}$[14-26] and $(NH_3)_5RuL^{2+,3+}$,[27-35] where L

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