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Comparison of the Influence of Saturated Nitrogen and Sulfur Donor Atoms on the Properties of Copper(II/I)–Macrocyclic Polyamino Polythiaether Ligand Complexes: Redox Potentials and Protonation and Stability Constants of Cu^IL Species and New Structural Data

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The relative influence of amine nitrogen and thiaether sulfur donor atoms upon the electrochemical behavior of the Cu(II/I) redox couple has been investigated by utilizing saturated macrocyclic polyamino polythiaether ligands of the 14-membered quadridentate and 15-membered quinquedentate series. The values of E^f (vs NHE) determined at 25 °C in aqueous solution containing 0.10 M perchlorate ion for the copper complexes formed with the specific ligands are as follows: [14]aneS_4, 0.58 V; [14]aneNS_3, 0.38 V; [14]aneN_2S_2, 0.04 V; [14]aneNSSN, −0.01 V; [14]aneN_3S, ≤−0.24 V (est); [14]aneN_4, −0.66 V (est); [15]aneS_5, 0.68 V; [15]aneNS_4, 0.46 V; [15]aneN_2S_3, 0.10 V. From the dependence of E^f on pH, it has also been possible to evaluate the mixed-mode protonation constants $K_{H1(Cu^IL)}{}^m$ for some of the Cu^IL complex species, for which the logarithmic values are as follows: [14]aneN_2S_2, 3.9; [15]aneNS_4, 4.17; [15]aneN_2S_3, 5.90. The electrochemical potentials show a fairly linear relationship with the value of x in each of the donor sets N_xS_{4-x} and N_xS_{5-x}. Empirical calculations suggest that the magnitude of the macrocyclic effect increases with each substitution of a saturated nitrogen donor atom for a thiaether sulfur donor atom. Combining the potentials with earlier measurements on the stability constants of the $Cu^{II}L$ complexes (which were linearly related to the value of x) permits calculation of the stability constants of the Cu^IL complexes which are found to be independent of the value of x for a specific ligand family with $K_{Cu^IL}' \approx 5 \times 10^{13}$ for the [14]aneN_xS_{4-x} series of complexes and $K_{Cu^IL}' \approx 4 \times 10^{15}$ for the [15]aneN_xS_{5-x} series. The only anomaly occurs for the case where $x = 0$ for which, in each series, the K_{Cu^IL}' value is about 100-fold smaller. These results demonstrate that Cu(I) exhibits little preference between saturated N and S donor atoms, contrary to the popular belief that sulfur donors stabilize the +1 oxidation state. Thus, the dependence of the Cu(II/I) potential on the relative number of N and S donor atoms is almost entirely a function of the preference of Cu(II) for amine nitrogen relative to thiaether sulfur as a donor atom. A crystallographic structure of the Cu^I([14]aneNS_3) complex reveals that all four ligand donor atoms are coordinated to Cu(I) in a flattened tetrahedral geometry. Crystal data [Mo Kα radiation (λ = 0.71073 Å)] at ambient temperature are as follows: $CuS_3NC_{10}H_{21}ClO_4$, triclinic crystal system, space group $P\bar{1}$, a = 8.468 (1) Å, b = 9.327 (2) Å, c = 12.311 (2) Å, α = 69.62 (2)°, β = 87.07 (1)°, γ = 67.60 (1)°, V = 838.9 (3) Å^3, Z = 2, R = 0.042, R_w = 0.056.

Introduction

The influence of the inner-coordination sphere upon the redox properties of the Cu(II/I) couple has received considerable attention, being stimulated, in large part, by the importance of this redox couple in enzymes. Much recent effort has been focused on the "blue" copper proteins, various members of which are involved in the photosynthetic chain in green plants. These proteins have unusual thermodynamic and spectral properties which are attributed to the unique structure and composition of the inner-coordination sphere at the active copper site.[2]

A large number of attempts have been made to generate low molecular weight model compounds which duplicate the properties of the type I copper center found in the blue copper proteins.[3] In addition, the properties of many other low molecular weight copper complexes have been examined to determine to what extent both the kinetic and thermodynamic properties of the Cu(II/I) redox couple are dependent upon geometry and/or the presence of soft donor atoms.[4] In assessing the influence of various parameters upon the Cu(II/I) redox potential, Addison[5] has developed an empirical relationship which assigns the contributions of various ligand parameters, including donor atoms and structural features, to the overall measured potential—and his efforts have been reasonably successful. However, such relationships are dependent upon the availability of data for a wide variety of copper complexes, and it is probable that both thermodynamic and kinetic behavior may be subject to subtle influences of the ligand morphology which have not yet been identified.

In earlier studies in our laboratory, we have carefully determined the formal potential values for a series of closely related open-chain and macrocyclic polythiaether complexes of copper and found that small differences are observed as a function of the cavity size in the macrocyclic species.[6,7] But the most striking characteristic of these complexes is their electron-transfer kinetic behavior which appears to involve a dual-pathway square scheme.[8,9] This mechanism implies that the electron-transfer process may be conformationally controlled in either the oxidation or the reduction half-cycle, resulting in the possibility of "gated" electron transfer.[10]

A number of our kinetic studies on the macrocyclic polythiaethers have been hampered by the very weak stability of the $Cu^{II}L$ species. In many cases it would be advantageous to modify these ligands in order to increase the $Cu^{II}L$ stability, if this could be

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[1] (a) Wayne State University. (b) University of Wisconsin—Eau Claire.

[2] For a recent review, see: Farver, O.; Pecht, I. *Coord. Chem. Rev.* **1989**, *94*, 17–45.

[3] Casella, L.; Gullotti, M.; Pintar, A.; Pinciroli, F.; Viganò, R.; Zanello, P. *J. Chem. Soc., Dalton Trans.* **1989**, 1161–1169 and references therein.

[4] One of the more interesting studies in this regard is the investigation of copper complexes which remain 5-coordinate in both the oxidized and reduced states: (a) Goodwin, J. A.; Wilson, L. J.; Stanbury, D. M.; Scott, R. A. *Inorg. Chem.* **1989**, *28*, 42–50. (b) Goodwin, J. A.; Stanbury, D. M.; Wilson, L. J.; Eigenbrot, C. W.; Scheidt, W. R. *J. Am. Chem. Soc.* **1987**, *109*, 2979–2991.

[5] Addison, A. W. *Inorg. Chim. Acta* **1989**, *162*, 217–220. Cf.: Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271–1285.

[6] Bernardo, M. M.; Schroeder, R. R.; Rorabacher, D. B. *Inorg. Chem.* **1991**, *30*, 1241–1247.

[7] (a) Rorabacher, D. B.; Martin, M. J.; Koenigbauer, M. J.; Malik, M.; Schroeder, R. R.; Endicott, J. F.; Ochrymowycz, L. A. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 167–202. (b) Dockal, E. R.; Jones, T. E.; Sokol, W. F.; Engerer, R. J.; Rorabacher, D. B.; Ochrymowycz, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 4322–4324.

[8] Bernardo, M. M.; Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1989**, *111*, 1224–1231.

[9] (a) Martin, M. J.; Endicott, J. F.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1987**, *26*, 3012–3022. (b) Rorabacher, D. B.; Bernardo, M. M.; Vande Linde, A. M. Q.; Leggett, G. H.; Westerby, B. C.; Martin, M. J.; Ochrymowycz, L. A. *Pure Appl. Chem.* **1988**, *60*, 501–508. (c) Vande Linde, A. M. Q.; Juntunen, K. L.; Mols, O.; Ksebati, M. B.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.*, in press.

[10] (a) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237–6243. (b) Brunschwig, B. S.; Sutin, N. *J. Am. Chem. Soc.* **1989**, *111*, 7454–7465.

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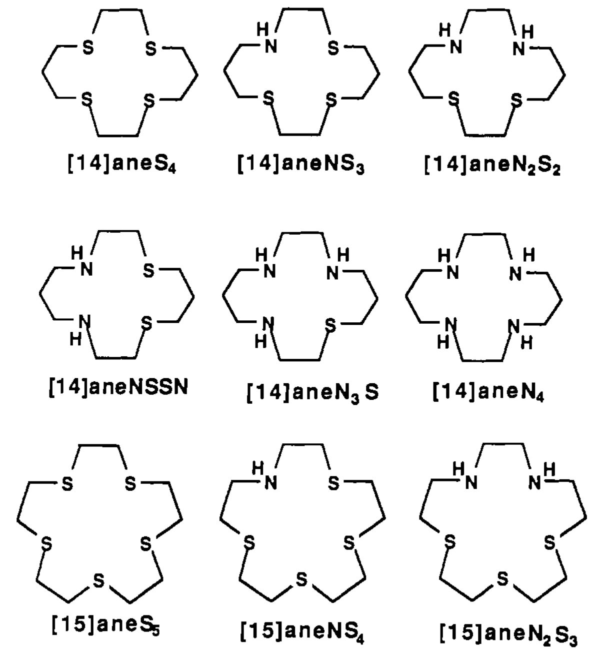

Figure 1. Ligands discussed in this work.

accomplished without seriously diminishing the Cu^{I}L stability and/or without lowering the Cu$^{II/I}$L potential to the point where the Cu^{I}L species is difficult to maintain in solution. An obvious ploy is to replace one or more of the thiaether sulfur donor atoms with a donor atom which forms stronger coordinate bonds to Cu(II).

In the current investigation, we have studied the comparative electrochemical behavior of a series of Cu(II/I)–polyamino polythiaether systems using conventional cyclic voltammetry (CV). In this work we have systematically substituted amine nitrogen donor atoms for the thiaether sulfur donor atoms in the previously reported macrocyclic polythiaethers. Although a number of workers have reported the results of studies on copper complexes containing mixed nitrogen–sulfur donor atoms, including macrocyclic compounds,[11] none of these efforts has focused on a systematic comparison of the effect of changing the donor atoms within a constant ligand framework.

In order to maintain a relatively constant coordination geometry, the ligands studied have been limited to two basic macrocyclic types: (i) 14-membered quadridentate macrocyclic ligands with alternating ethylene and trimethylene bridging groups, a structure which has been shown to provide an optimal cavity size to accommodate the Cu(II) ion[12] but a structure for which previous evidence has suggested the rupture of one metal–donor bond may occur upon reduction to Cu(I);[13] and (ii) closely related 15-membered quinquedentate macrocyclic ligand systems involving all ethylene bridging groups, which have been shown to form distorted 5-coordinate square-pyramidal Cu(II) complexes and slightly distorted 4-coordinate tetrahedral Cu(I) complexes.[14] The protonation constants and Cu(II) complex stability constants for the same series of polyamino polythiaether ligand systems included in the current study have recently been reported as well,[15] facilitating the interpretation of the electrochemical measurements generated in this work.

The five macrocyclic ligands investigated in the current 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), 1,4,7,10-tetrathia-13-azacyclopentadecane ([15]aneNS$_4$), and 1,4,7-trithia-10,13-diazacyclopentadecane ([15]aneN$_2$S$_3$). Of these ligands, only the copper complex of [14]aneN$_2$S$_2$ has been previously studied electrochemically, and that study involved only the straightforward determination of the Cu(II/I) potential.[11a] All five ligands are depicted in Figure 1 along with the corresponding polythiaether ligands with which these mixed-donor species are compared. Also included in this figure are the related ligands [14]aneN$_3$S and [14]aneN$_4$ (i.e., cyclam), for which estimated data are also presented in this work.

Experimental Section

Instrumental Methods. The experimental procedures utilized were essentially identical to those described previously[8] and, therefore, are summarized only briefly here. The instrumentation consisted of a Princeton Applied Research (PAR) Model 175 universal programmer, a PAR Model 173 potentiostat equipped with a Model 179 digital coulometer, a current-to-voltage converter, and an interfaced minicomputer. Potentials were measured against the aqueous saturated sodium chloride reference electrode (SSCE, E^f = 0.236 V vs NHE)[16] and were not corrected for junction potentials. The auxiliary electrode consisted of a platinum coil. The working electrode consisted of glassy carbon press-fitted onto a Kel-F shroud (Bioanalytical Systems). Extreme care was taken in the pretreatment of this electrode based on the method recommended by Rusling and co-workers.[17]

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

Reagents. Preparation and purification of Cu(ClO$_4$)$_2$·6H$_2$O and standardization of its aqueous solutions have been previously described.[18] The synthesis of the five macrocyclic polyamino polythiaether ligands will be presented elsewhere.[19] Solutions of these ligands were standardized either by pH titration or, more generally, by spectrophotometric absorbance measurements in the presence of excess aquocopper(II) ion. Copper(II) complex solutions were prepared by dissolving recrystallized copper perchlorate and the macrocyclic ligand in distilled, deionized water. When desired, these solutions were reduced by controlled-potential electrolysis to prepare the corresponding Cu^{I}L solutions. Ionic strength was controlled by the addition of reagent grade HClO$_4$ (G. F. Smith Chemical Co.) or NaClO$_4$, the latter salt prepared by the slow addition of HClO$_4$ to a concentrated solution of reagent grade NaOH and then recrystallized twice. Crystals of [Cu^I([14]aneNS$_3$)]ClO$_4$, suitable for resolution by X-ray diffractometry, were grown from a mixture of 80% methanol–20% water (w/w).

Crystallography. Single-crystal X-ray diffraction measurements were performed on a Nicolet R3 automated diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator at ambient

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(11) (a) Balakrishnan, K. P.; Kaden, T. A.; Siegfried, L.; Zuberbühler, A. D. *Helv. Chim. Acta* **1984**, *67*, 1060–1069. (b) Balakrishnan, K. P.; Riesen, A.; Zuberbühler, A. D.; Kaden, T. A. *Acta Crystallogr.* **1990**, *C46*, 1236–1238 and references therein. (c) McCrindle, R.; Ferguson, G.; McAlees, A. J.; Parvez, M.; Ruhl, B. L.; Stephenson, D. K.; Wieckowski, T. *J. Chem. Soc., Dalton Trans.* **1986**, 2351–2359. (d) Louis, R.; Arnaud-Neu, F.; Weiss, R.; Schwing-Weill, M. J. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 31–35. (e) Addison, A. W.; Burke, P. J.; Henrick, K.; Rao, T. N.; Sinn, E. *Inorg. Chem.* **1983**, *22*, 3645–3653. (f) Alberts, A. H.; Lehn, J.-M.; Parker, D. *J. Chem. Soc., Dalton Trans.* **1985**, 2311–2317. (g) Kodama, M.; Koike, T.; Hoshiga, N.; Machida, R.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1984**, 673–678.

(12) Glick, M. D.; Gavel, D. P.; Diaddario, L. L.; Rorabacher, D. B. *Inorg. Chem.* **1976**, *15*, 1190–1193.

(13) Dockal, E. R.; Diaddario, L. L.; Glick, M. D.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1977**, *99*, 4530–4532.

(14) Corfield, P. W. R.; Ceccarelli, C.; Glick, M. D.; Moy, I. W. Y.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1985**, *107*, 2399–2404.

(15) Westerby, B. C.; Juntunen, K. L.; Leggett, G. H.; Pett, V. B.; Koenigbauer, M. J.; Purgett, M. D.; Taschner, M. J.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1991**, *30*, 2109–2120.

(16) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

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

(18) Diaddario, L. L.; Zimmer, L. L.; Jones, T. E.; Sokol, L. S. W. L.; Cruz, R. B.; Yee, E. L.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3511–3520.

(19) Purgett, M. D.; Taschner, M. J.; Kubiak, G.; Reed, P. R.; Moy, I. W.-Y.; Bloomquist, D. A.; Ochrymowycz, L. A. To be submitted for publication.

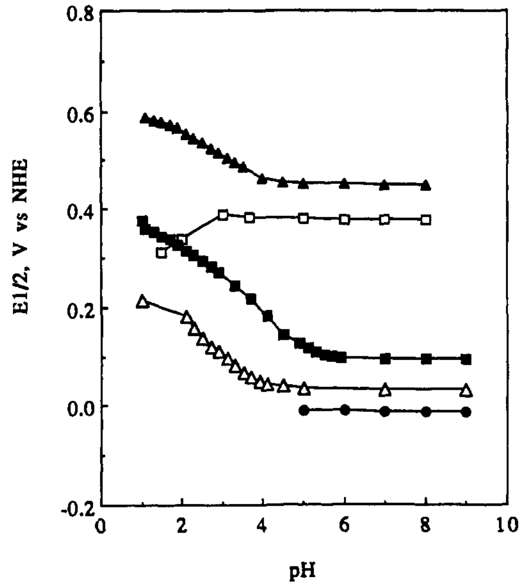

Figure 2. Plots of half-wave potential as a function of pH for $Cu^{II/I}L$ systems at a glassy-carbon electrode in aqueous solution at 25 °C: □ = [14]aneNS$_3$, △ = [14]aneN_2S_2, ● = [14]aneNSSN, ▲ = [15]aneNS$_4$, ■ = [15]aneN_2S_3.

temperature. Details of data collection: scan method, $\theta/2\theta$; scan range, 1.0° below $K\alpha_1$ to 1.0° above $K\alpha_2$; scan rate variable, 2–5° min^{-1}; ratio of background/scan time, 0.5. The structure was solved by Patterson methods and refined in a full matrix with the programs of SHELX-76.[20] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in observed positions and held invariant. No correction for secondary extinction was made. Neutral-atom scattering factors and corrections for anomalous dispersion were from ref 21. Abbreviated crystallographic data for $[Cu^I([14]aneNS_3)]ClO_4$ follow: formula $CuS_3NC_{10}H_{21}ClO_4$, fw 414.47, colorless irregular crystals, 0.50 × 0.42 × 0.40 mm^3, coated with a thin layer of epoxy to retard oxidation, triclinic crystal system, space group $P\bar{1}$, $a = 8.468$ (1) Å, $b = 9.327$ (2) Å, $c = 12.311$ (2) Å, $\alpha = 69.62$ (2)°, $\beta = 87.07$ (1)°, $\gamma = 67.60$ (1)°, $V = 838.9$ (3) Å^3, $Z = 2$, $F_{000} = 428$ e, d(calcd) = 1.641 g cm^{-3}, 2θ range 6–50°, hkl ranges $0 \leq h \leq 11$, $-12 \leq k \leq 12$, $-15 \leq l \leq 15$, 6159 total data collected which included a complete set of Friedel pairs, 2294 observed unique data ($R_{av} = 0.008$) with $I \geq 3\sigma(I)$, $\mu = 18.33$ cm^{-1}, absorption corrections by empirical methods[22] yielding transmission coefficients 0.678–0.514, final conventional R value 0.042, final weighted R value 0.056, weight $(\sigma_F + 0.0003F^2)^{-2}$. Lattice constants were derived from 25 high-angle ($2\theta > 20°$) reflections.

Results

Cyclic Voltammetric Measurements. Cyclic voltammetric measurements were made on aqueous $Cu^{II}L$ solutions at 25 °C for all five ligand systems, with limited additional measurements on Cu^IL solutions. In all studies, the sweep rate was varied from 0.010 to at least 0.100 V s^{-1}, generally covering the range from pH 1.0 to 8.0 or 9.0 in increments of approximately 1 pH unit. For the systems involving [14]aneN_2S_2, [15]aneNS$_4$, and [15]aneN_2S_3, more extensive studies were conducted in the range of pH 1.0–5.0 at increments of 0.2–0.4 pH unit to examine more closely the changes in behavior which occur in this region. Since, in all cases, the systems showed essentially reversible behavior at slower sweep rates, the half-wave potentials were determined as the average of the values obtained at scan rates of 0.010, 0.020, 0.050, and 0.100 V s^{-1}.

For $Cu^{II}([14]aneNS_3)$ solutions, the $E_{1/2}$ value remained essentially invariant down to pH 3.6 with electrochemically reversible characteristics. At pH 3.0, the potential was observed to increase slightly but then plummeted at lower pH values (Figure 2, open squares). This low pH behavior suggests that the protonated $Cu^{II}HL$ species rapidly dissociates in solution.

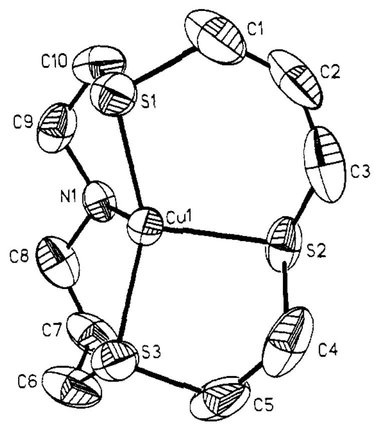

Figure 3. Ortep drawing of the cationic unit of $[Cu^I([14]aneNS_3)]ClO_4$ showing the labeling scheme for atoms.

For $Cu^{II}([14]aneN_2S_2)$ solutions, the electrochemical behavior was again virtually reversible over the range of pH 5.0–9.0 for sweep rates up to 0.100 V s^{-1}. Below pH 5.0, the voltammograms showed quasi-reversible behavior and the $E_{1/2}$ values were observed to shift to more positive potentials (Figure 2, open triangles). An extended CV study at pH 1.0 revealed the development of a second anodic peak at more positive potentials and the emergence of a cathodic shoulder. However, due to the known slow equilibration of the $Cu^{II}([14]aneN_2S_2)$ species under these acidic conditions[15] (vide infra), the significance of this behavior cannot be established.

Studies on $Cu^{II}([14]aneNSSN)$ were limited to pH 5.0–8.7, where the system already exhibited a slight degree of quasi-reversibility. The $E_{1/2}$ value remained constant over this interval at −0.01 V vs NHE (Figure 2, solid circles). Measurements at lower pH values were precluded by the interference of the $Cu(aq)^{2+}/Cu^0$ redox process with observation of the cathodic peak.

The cyclic voltammograms for $Cu^{II}([15]aneNS_4)$ solutions were nearly reversible over the entire range of pH 1.0–8.0 for scan rates of 0.010–0.100 V s^{-1}. Even at scan rates up to 10.0 V s^{-1}, the degree of observed quasi-reversibility was relatively small. Below pH 5.0, the $E_{1/2}$ values were observed to increase (Figure 2, solid triangles) in a manner similar to that observed for $Cu^{II}([14]aneN_2S_2)$ solutions.

For $Cu^{II}([15]aneN_2S_3)$ solutions, the cyclic voltammograms were essentially reversible at scan rates of 0.01–0.10 V s^{-1} over the range of pH 6.0–9.0. Below pH 6.0, the $E_{1/2}$ value increased (Figure 2, solid squares), as observed for the [14]aneN_2S_2 and [15]aneNS$_4$ systems. At pH 1.0, a second anodic peak was observed to develop at scan rates of 0.20–1.0 V s^{-1}. This latter phenomenon is reminiscent of the behavior previously observed for the $Cu^{II/I}([14]aneS_4)$ system at low temperature and/or fast sweep rates which we have attributed to slow conformational changes.[8,23] However, the fact that this behavior is limited to very low pH in the [15]aneN_2S_3 system suggests that protonated species are involved and the similarities to the [14]aneS$_4$ system may be fortuitous.

Determination of Crystal Structure for $[Cu^I([14]aneNS_3)]ClO_4$. The atomic labeling scheme for the $Cu^I([14]aneNS_3)$ cation is shown in Figure 3. The structure consists of one independent cation and one independent anion with all atoms occupying general positions. There are no unusual close contacts between residues. Fractional atomic coordinates are listed in Table I. Bond lengths and angles for the cation are presented in Table II. The copper atom lies in an approximately tetrahedral environment, being coordinated to the three sulfur and one nitrogen donor atoms. The chelate bite angles are S–Cu–S = 95.26 (7)° (en linkage) and 110.44 (8)° (tm linkage) and S–Cu–N = 91.2 (2)° (en linkage) and 109.2 (1)° (tm linkage). The [14]aneNS$_3$ ligand is not

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(20) Sheldrick, G. M. SHELX-76. University Chemical Laboratory, Cambridge, England, 1976.

(21) *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4 (present distributor: D. Reidel, Dordrecht, The Netherlands).

(22) Sheldrick, G. M. SHELXTL. University of Göttingen, Germany, 1978.

(23) Robandt, P. V.; Schroeder, R. R.; Rorabacher, D. B. To be submitted for publication.

Table I. Atomic Positional Parameters for $[Cu^I([14]aneNS_3)]ClO_4$

atom	*x*	*y*	*z*	occ[a]
Cu	0.46440 (6)	0.49122 (6)	0.20613 (4)	
S1	0.3235 (2)	0.3958 (2)	0.1160 (1)	
C1	0.254 (1)	0.250 (1)	0.2312 (8)	
C2	0.247 (1)	0.258 (1)	0.3505 (8)	
C3	0.403 (1)	0.2144 (9)	0.4191 (7)	
S2	0.4514 (2)	0.3918 (2)	0.4021 (1)	
C4	0.6854 (9)	0.303 (1)	0.4360 (5)	
C5	0.67581 (8)	0.428 (2)	0.3733 (6)	
S3	0.7293 (2)	0.4872 (2)	0.2174 (1)	
C6	0.6867 (8)	0.711 (1)	0.1636 (7)	
C7	0.503 (1)	0.8290 (9)	0.1687 (8)	
C8	0.3721 (9)	0.8518 (7)	0.0831 (6)	
N1	0.2946 (5)	0.7321 (4)	0.1235 (3)	
C9	0.1894 (7)	0.7316 (8)	0.0307 (4)	
C10	0.1346 (7)	0.5909 (9)	0.0748 (6)	
Cl1	0.0705 (2)	0.0800 (2)	0.7011 (1)	
O1	0.084 (2)	0.080 (2)	0.5861 (8)	0.63
O2	−0.015 (1)	0.247 (1)	0.690 (1)	0.63
O3	0.240 (2)	−0.02 (1)	0.753 (1)	0.63
O4	−0.039 (2)	0.006 (2)	0.769 (1)	0.63
O5	0.065 (2)	0.106 (2)	0.811 (1)	0.63
O6	0.241 (3)	−0.005 (6)	0.710 (3)	0.63
O7	0.052 (4)	0.238 (4)	0.621 (3)	0.32
O8	0.005 (3)	0.008 (4)	0.647 (4)	0.32
O9	−0.021 (6)	0.001 (6)	0.723 (3)	0.20

[a] If not otherwise listed, occupancy is 1.0.

Table II. Bond Distances (Å) and Angles (deg) for the Cationic Unit of $[Cu^I([14]aneNS_3)]ClO_4$

Cu1–S1	2.254 (2)	S3–C6	1.85 (1)
Cu1–S2	2.277 (2)	N1–C8	1.44 (1)
Cu1–S3	2.240 (2)	N1–C9	1.486 (9)
Cu1–N1	2.061 (5)	C1–C2	1.49 (2)
S1–C10	1.829 (8)	C2–C3	1.44 (2)
S1–C1	1.84 (1)	C4–C5	1.49 (2)
S2–C3	1.80 (1)	C6–C7	1.54 (1)
S2–C4	1.839 (7)	C7–C8	1.47 (1)
S3–C5	1.80 (1)	C9–C10	1.47 (1)
Cu1–S1–C10	92.0 (3)	S1–C10–C9	109.5 (4)
Cu1–S1–C1	106.7 (4)	S1–C1–C2	118.9 (9)
Cu1–S2–C3	101.1 (4)	S2–C3–C2	112.3 (9)
Cu1–S2–C4	94.1 (4)	S2–C4–C5	110.3 (7)
Cu1–S3–C5	97.5 (3)	S3–C5–C4	112.4 (9)
Cu1–S3–C6	101.7 (1)	S3–C6–C7	116.5 (7)
Cu1–N1–C8	114.7 (4)	N1–C8–C7	113.3 (8)
Cu1–N1–C9	107.3 (4)	N1–C9–C10	110.5 (7)
S1–Cu1–S2	110.44 (8)	C10–S1–C1	103.5 (4)
S2–Cu1–S3	95.26 (7)	C3–S2–C4	103.5 (5)
S3–Cu–N1	109.2 (1)	C5–S3–C6	103.3 (6)
N1–Cu1–S1	91.2 (2)	C8–N1–C9	113.8 (6)
S1–Cu1–S3	137.25 (8)	C1–C2–C3	120.5 (9)
S2–Cu1–N1	114.2 (2)	C4–C5–C6	103.3 (6)

sufficiently large or flexible to accommodate ideal tetrahedral geometry around the copper atom. Consequently, the ligand atoms are concentrated to one side of the complex, leaving an exposed region (S1–Cu1–S3 = 137.25 (8)°, Figure 4) which might be susceptible to additional coordination or attack in solution. However, in the solid state there are no close intermolecular contacts to the Cu atom. The dihedral angles in the first coordination sphere also describe the inability of the ligand to wrap ideally. The angle between the two five-membered chelate rings defined by the N1–Cu1–S1 plane and the opposing S2–Cu1–S3 plane is 79.2 (1)°, while the angle between the two six-membered chelate rings, i.e., between the N1–Cu1–S3 plane and the S1–Cu1–S2 plane, is 70.3 (1)°. Both of these values are considerably less than the ideal tetrahedral dihedral angle of 90°. Overall, the geometry can be viewed as an asymmetrically flattened tetrahedron with bond angle opening occurring at the S1–Cu–S3 angle (137.25 (8)°) and, to a lesser extent, at the N1–Cu–S2 angle (114.2 (2)°).

The Cu–S bond lengths are not uniform and likely reflect both the strain in the complex in accommodating a (necessarily) shorter Cu–N bond and the differing lengths of the carbon bridges between donor atoms. The two Cu–S bonds flanking N in the macrocyclic ring are significantly shorter than the remaining Cu–S2 length (2.25 and 2.24 Å vs 2.28 Å). The carbon atoms possess high thermal parameters, which indicates some degree of conformational disorder in these rings.

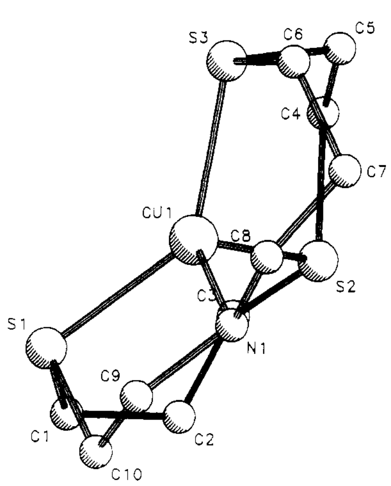

Figure 4. Side view of the cationic unit of $[Cu^I([14]aneNS_3)]ClO_4$ showing the exposed region above the Cu atom.

The perchlorate anion is principally described by atoms Cl1 and O1–O4. These Cl–O lengths range from 1.40 (1) to 1.43 (1) Å, and bond angles are in the range 101.7–117.7 (8)°. However, there was significant leftover electron density in this region and high thermal parameters for O1–O4 when they were given full occupancy, indicative of the common perchlorate disorder problem. Refinement of the model proceeded best with a number of partial oxygens in this region. The O1–O9 oxygens listed in Table I represent fractional perchlorate oxygens and are given occupancies as listed, the total summing to four oxygen atoms.

Discussion

Structure of $Cu^{II}L$ and Cu^L Species. Previous work in our laboratory has demonstrated that conformational changes are of importance in controlling the electron-transfer kinetics of $Cu^{II/I}([14]aneS_4)$.[8,9] This has created a heightened interest in the specific structures associated with the oxidized and reduced species. We have earlier reported the results of X-ray diffractometric determinations of the crystal structures of both $[Cu^{II}([14]aneS_4)](ClO_4)_2$ and $[Cu^I([14]aneS_4)]ClO_4$.[12,13,24] The $Cu^{II}L$ structure was found to be tetragonal, with the four sulfur donor atoms coplanar with the copper atom and two perchlorate ions loosely coordinated at the axial sites. For $Cu^I([14]aneS_4)$, however, the structure was found to be polymeric, with each Cu(I) ion coordinated to four thiaether sulfur donor atoms, three of the sulfurs being from one ligand and the fourth from an adjacent ligand, this arrangement continuing in an (infinite) chain with each copper atom in a tetrahedral environment.

Kinetic measurements have indicated that the $Cu^I([14]aneS_4)$ species is not polymeric in dilute aqueous or methanolic solutions.[9a,25] Combining this information with the earlier crystal structure suggested that three sulfur atoms and one solvent molecule might be presumed to form the inner-coordination sphere of $Cu^I([14]aneS_4)$ in solution. Recent NMR measurements on this species have revealed that all four Cu^I–S bonds appear to be equivalent on the NMR time scale in solution.[26] This evidence suggests either that the ligand is capable of maintaining all four Cu–S bonds upon reduction of the copper or that, if one Cu–S bond is ruptured on a time-averaged basis, the equilibration of all four Cu–S bonds is rapid in solution.

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(24) Diaddario, L. L., Jr.; Dockal, E. R.; Glick, M. D.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1985**, *24*, 356–363.

(25) Meagher, N. E.; Juntunen, K. L.; Rorabacher, D. B. To be submitted for publication.

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

Table III. Half-Wave Potentials for Copper–Polyamino Polythiaether Complexes and Protonation Constant Values for $Cu^{I}L$ Species in Aqueous Solution at 25 °C, $\mu = 0.10$

complexed ligand	$E_{1/2}$(measd),[b] V (vs NHE)	empirical $E_{1/2}$, V (vs NHE)[a]		$Cu^{I}L$ protonation	
		lit. ΔE_L parameters	modified ΔE_L parameters	log $K_{H1}{}^{m}$	log $K_{H2}{}^{m}$
$[14]aneS_4$	0.58[c]	0.63	0.60		
$[14]aneNS_3$	0.38 (pH >3.5)	0.41	0.29	<3.0	
$[14]aneN_2S_2$	0.04 (pH >5.0) *0.08*[e]	0.19	−0.01	3.9	[2.9][d]
[14]aneNSSN	−0.01 (pH >5.0)	0.19	−0.01	<5.0	
$[14]aneN_3S$	≤−0.24 (est)[f]	−0.02	−0.32		
$[14]aneN_4$	−0.66 (est)[g]	−0.24	−0.62		
$[15]aneS_5$	0.68[c]				
$[15]aneNS_4$	0.457 (pH >5.0)			4.17	
$[15]aneN_2S_3$	0.098 (pH >6.0)			5.90	

[a] Values calculated from eq 3 using $E_{aq}{}^{\circ\prime} = 0.13$ V; literature ΔE_L parameters (in V) are those proposed by Addison:[5] +0.141 for each thiaether sulfur donor atom, −0.075 for each aliphatic nitrogen, +0.024 for macrocyclic ligands, −0.046 for each 5-membered ring. Modified parameters (V): +0.170 for each thiaether donor atom, −0.12 for the S_4 macrocyclic ligand and decreased by 0.06 for each substitution of an aliphatic nitrogen, other parameters unchanged. [b] All experimentally determined $E_{1/2}$ values are believed to be accurate to within ±0.01 V (see ref 6). [c] Previously reported $E_{1/2}$ values for $Cu^{II/I}([14]aneS_4)$ and $Cu^{II/I}([15]aneS_5)$ were 0.01 V more positive than those listed here due to a slight error in correcting for the potential of the SSCE reference electrode.[6] [d] The value of log $K_{H2}{}^{m}$ obtained for the $Cu^{I}([14]aneN_2S_2)$ complex may be erroneous due to a failure to achieve equilibrated conditions (see text). [e] Value for 20 °C, $\mu = 0.20$ (Na_2SO_4).[11a] [f] Value estimated using eq 13 assuming $K_{Cu^{II}L}{}' \geq 1 \times 10^{20}$ and $K_{Cu^{I}L}{}' \approx 4 \times 10^{13}$ (see text). [g] Values estimated from the trend of methanolic potentials of copper complexes with related 14-membered macrocyclic N_4 ligands containing unsaturated nitrogens[31] assuming $E^{f}{}_{H_2O} = E^{f}{}_{MeOH} - 0.060$ V.[5]

The resolution of the crystal structure for $[Cu^{I}([14]aneNS_3)]ClO_4$, as a part of the current study, provides independent evidence for the ability of a 14-membered quadridentate ligand to maintain four coordinate bonds to a single Cu(I) ion in a monomeric species. It is also noteworthy that a similar $Cu^{I}L$ structure has been observed for a $[14]eneN_2(imino)S_2$ complex with Cu^{I}, viz., (6,7,15,16-tetrahydrodibenzo[*f*,*m*][1,8,4,11]dithiadiazacyclotetradecine)copper(I).[27] The similarities in ligand conformation are remarkable in light of the rigidity requirements of the imino and dibenzo groups. Other examples of similar coordination geometry in Cu(I)–N,S complexes, in which the copper is in a severely distorted tetrahedron, can be found with tripodal ligands,[28] 14-and 16-membered thia–imino macrocycles,[29] and, occasionally, in bis(thia ligand) complexes where the ligands are without constraint with regard to each other.[30]

The fact that the distortions from regular tetrahedral geometry in $Cu^{I}([14]aneNS_3)$ are attributable to ligand constraints is evident by comparison to the structure of the $Cu^{I}([16]aneN_2S_2)^+$ cation,[11b] where the macrocyclic ligand cavity is expanded by two carbon atoms. In this latter species, the bond angles are closer to ideal tetrahedral values (102.1–120.5°) and the dihedral angle between the two donor planes is orthogonal (89.6°). Nonetheless, the bond distances of this latter compound are in close agreement with those reported in the current work for $Cu^{I}([14]aneNS_3)$.

It is presumed that the strained nature of the $Cu^{I}L$ complex noted above is common to all 14-membered macrocyclic species. On this basis, it is speculated that this may account for the fact that, to date, only these species have shown direct electrochemical evidence of our proposed square-scheme mechanism for $Cu^{II/I}L$ electron-transfer reactions which involves conformational interconversions to metastable intermediates of both the $Cu^{II}L$ and $Cu^{I}L$ species.[8] The greater flexibility of the larger macrocycles may make such conformational changes too rapid to be detectable whereas the more rigid smaller macrocycles may result in conformational conversions which are too slow to be observed on the measured time scale.

Potential Values. At high pH values and slow scan rates, the cyclic voltammetric curves for all copper–polyamino thiaether complexes studied show nearly reversible behavior which is independent of pH in this region. Under these conditions, we may assume that the experimental $E_{1/2}$ values approximate the formal potentials for these systems corresponding to the half reaction

$$Cu^{II}L + e^- \rightleftharpoons Cu^{I}L \quad E^{f} \tag{1}$$

as represented by the Nernst equation written in the form

$$E = E^{f} - \frac{2.303RT}{n\mathcal{F}} \log \frac{[Cu^{I}L]}{[Cu^{II}L]} \tag{2}$$

These $E_{1/2}$ values are listed in Table III for all five systems included in this work. Also included in this table are the previously reported values for the corresponding ligand systems containing all sulfur atoms.

Although we were unable to obtain suitable $E_{1/2}$ values for the copper complexes formed with $[14]aneN_3S$ and $[14]aneN_4$, we have estimated the value for the latter system from literature values of the methanolic potentials for $Cu^{II/I}(Me_4[14]tetraeneN_4)$ and $Cu^{II/I}(Me_2[14]dieneN_4)$[31] by assuming that each substitution of a saturated nitrogen for an unsaturated nitrogen (and the loss of two ring methyl groups) will cause a regular progression in the E^{f} value. Combining this approach with Addison's correction factor for correlating methanolic and aqueous potentials ($E_{aq}{}^{f} = E_{MeOH}{}^{f} - 0.06$ V)[5] yields an estimated aqueous potential for $Cu^{II/I}([14]aneN_4)$. With the availability of aqueous E^{f} values for each of the other 14-membered macrocyclic ligand systems, it has then proved possible to establish an upper limit to the E^{f} value for the $Cu^{II/I}([14]aneN_3S)$ system (vide infra). Both of these estimated E^{f} values are included in Table III.

Empirical Calculation of Potential Values. It is evident from the data in Table III that each substitution of a nitrogen donor atom for a thiaether sulfur donor atom causes a fairly regular decrease in the $E_{1/2}$ value for $Cu^{II/I}L$, amounting to an average of about 0.30 V per nitrogen. This regular decrease is consistent with Addison's proposal that, to a fair degree of accuracy, an empirical relationship can be established in which various ligand features are assigned quantitative values relative to their influence upon the Cu(II/I) potential as expressed by the relationship[5]

$$E_{1/2} = E_{aq}{}^{\circ} + \sum(n\Delta E_L) \tag{3}$$

In eq 3, $E_{aq}{}^{\circ}$ is the potential of the aqueous Cu(II/I) redox couple, ΔE_L represents the change in the Cu(II/I) potential caused by

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(27) Wainwright, K. P.; Patalinghug, W.; Skelton, B. W.; White, A. H.; Healy, P. C. *J. Chem. Soc., Dalton Trans.* **1988**, 2301–2305.

(28) (a) Karlin, K. D.; Dahlstron, P. L.; Stanford, M. L.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1979**, 465–467. (b) Karlin, K. D.; Dahlstron, P. L.; Hyde, J. R.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1980**, 906–908.

(29) Martin, J. W. L.; Organ, G. J.; Wainwright, K. P.; Weerasuria, K. D. V.; Willis, A. C.; Wild, S. B. *Inorg. Chem.* **1987**, *26*, 2963–2968.

(30) Lucas, C. R.; Shuang, L.; Newlands, M. J.; Charland, J.-P.; Gage, E. J. *Can. J. Chem.* **1988**, *66*, 1506–1512.

(31) Fabbrizzi, L.; Lari, A.; Poggi, A.; Seghi, B. *Inorg. Chem.* **1982**, *21*, 2083–2085. $Me_4[14]tetraeneN_4$ and $Me_2[14]dieneN_4$ represent 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene and 2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene, respectively.

various ligand features (such as type of donor atom, number of five-membered chelate rings, etc.), and *n* represents the number of times each feature occurs for a specific ligand species. In our calculations, we have replaced Addison's value of $E_{aq}° = 0.155$ V by a corrected concentration potential value of $E_{aq}°' = 0.13$ as determined by applying the extended Debye–Hückel equation to 0.10 M ionic strength.

The empirical $E_{1/2}$ values calculated using eq 3 are tabulated in the third column of Table III. It is clear that the use of Addison's parameter values yields reasonable agreement with the experimental $E_{1/2}$ values only for ligand systems containing no more than one aliphatic nitrogen. Since Addison's parameters were derived from computer correlations of many compounds, it is presumed that, for the most part, they have reasonable validity. However, the most questionable parameter is that generated for the macrocyclic effect for which Addison has assigned a value of $\Delta E_L = 0.024$. In previous studies,[32] we have noted that the macrocyclic effect for Cu^{II}([14]aneS_4) relative to corresponding acyclic complexes is 10^2 for 14-membered ring ligands, while there appears to be no macrocyclic effect for the corresponding Cu(I) species. This should result in a ΔE_L value of about −0.12 V for the macrocyclic effect.[33] Similarly, the macrocyclic effect has been evaluated as approximately 10^6 for Cu^{II}([14]aneN_4),[34] leading to a macrocyclic ΔE_L value of about −0.36 V (again assuming no macrocyclic effect for Cu^IL). Thus, it is clear that the macrocyclic ligand parameter derived by Addison should not be a constant throughout the current ligand series. We have made revised empirically calculated $E_{1/2}$ values by assigning a variable value for the macrocyclic ligand parameter, starting with −0.12 V for the [14]aneS_4 system and decreasing this parameter by 0.06 V for each substitution of an aliphatic nitrogen for a thiaether sulfur donor atom. To compensate for the decrease in the macrocyclic parameter, the ΔE_L parameter for each thiaether donor atom has been increased to +0.170 V (as compared to Addison's value of +0.141 V, which was based primarily on macrocyclic polythiaether ligand complexes). These revised empirical $E_{1/2}$ values are listed in the fourth column of Table III and, on the whole, are seen to be in reasonably close agreement with the experimentally determined values.

As noted above, the magnitude of the macrocyclic effect has been evaluated previously only for the two extreme cases (i.e., S_4 vs N_4). The reasonable agreement of the empirically calculated $E_{1/2}$ values, using our modified parameters, suggests that the macrocyclic effect does become progressively larger as each nitrogen is incorporated. Although it is unlikely that this is a completely smooth trend, the implication of this fit is that the substitution of each nitrogen for a thiaether sulfur increases the preorganization of the ligand conformation toward favorable coordination to Cu(II); i.e., the lone-pair electrons on each sulfur atom tend to be oriented away from the ligand cavity (exo), while those on the nitrogen atoms tend to be oriented into the cavity (endo)—in agreement with the conclusions of other studies.[35] As noted below, there is no corresponding influence on Cu(I) coordination.

Within the limits of experimental error, it is noted that the potentials for the quinquedentate 15-membered macrocyclic ligand complexes remain approximately 0.1 V more positive than those for the corresponding quadridentate 14-membered macrocyclic systems. However, the data for this ligand series are too limited to permit a detailed analysis of the trends involved.

Protonation of Copper(I) Complexes. The shift in the redox potentials of the mixed-donor systems toward more positive values at low pH can best be explained in terms of the formation of protonated complex species according to the reactions of the type

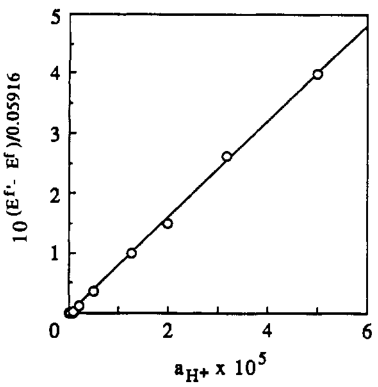

Figure 5. Plot of eq 9 for $Cu^{II/I}$([15]aneN_2S_3).

$$Cu^IL + H^+ \rightleftharpoons Cu^IHL \quad K_{H1(Cu^IL)} \tag{4}$$

$$Cu^IHL + H^+ \rightleftharpoons Cu^IH_2L \quad K_{H2(Cu^IL)} \tag{5}$$

with corresponding reactions also conceivable for the $Cu^{II}L$ complexes.[36] The reciprocal mole fractions of the unprotonated complex species may be represented as (using Ringbom's convention)[37]

$$\alpha_{Cu^IL} = \frac{[Cu^IL] + [Cu^IHL] + [Cu^IH_2L]}{[Cu^IL]} = 1 + K_{H1(Cu^IL)}{}^m a_{H^+} + K_{H1(Cu^IL)}{}^m K_{H2(Cu^IL)}{}^m (a_{H^+})^2 \tag{6}$$

$$\alpha_{Cu^{II}L} = \frac{[Cu^{II}L] + [Cu^{II}HL] + [Cu^{II}H_2L]}{[Cu^{II}L]} = 1 + K_{H1(Cu^{II}L)}{}^m a_{H^+} + K_{H1(Cu^{II}L)}{}^m K_{H2(Cu^{II}L)}{}^m (a_{H^+})^2 \tag{7}$$

where the protonation constants are given as mixed-mode constants (designated by the superscript "m") involving the activity of hydrogen ion, all other species being in molar concentrations. Appropriate substitution of eqs 6 and 7 into eq 2 yields

$$E^{f'} = E^f - \frac{2.303RT}{n\mathcal{F}} \log \frac{\alpha_{Cu^IL}}{\alpha_{Cu^{II}L}}$$

$$E^{f'} = E^f - \frac{2.303RT}{n\mathcal{F}} \times \log \frac{[1 - K_{H1(Cu^IL)}{}^m a_{H^+} + K_{H1(Cu^IL)}{}^m K_{H2(Cu^IL)}{}^m (a_{H^+})^2]}{[1 + K_{H1(Cu^{II}L)}{}^m a_{H^+} + K_{H1(Cu^{II}L)}{}^m K_{H2(Cu^{II}L)}{}^m (a_{H^+})^2]} \tag{8}$$

where E^f represents the previously listed $E_{1/2}$ potential values at high pH, where no complex protonation occurs (i.e., where $\alpha_{Cu^IL} = \alpha_{Cu^{II}L} = 1$) and $E^{f'}$ represents the measured pH-dependent formal potential. Since the measured formal potential increases with increasing acidity, it is apparent that the Cu^IL complex is undergoing protonation to a greater extent that is the oxidized species. Therefore, *for the specific limiting condition* in which the Cu^IL species has begun to add a single H^+ ion and $Cu^{II}L$ is still unprotonated, the denominator in the logarithmic term of eq 8 may be considered to be unity and the term in the numerator involving $(a_{H^+})^2$ may be ignored. Equation 8 may then be rearranged to the simple form

$$10^{(E^{f'}-E^f)n\mathcal{F}/(2.303RT)} = 1 + K_{H1(Cu^IL)}{}^m a_{H^+} \tag{9}$$

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

(33) This is in close agreement with the 0.10 V difference in the experimentally determined E^f values for $Cu^{II/I}$([14]aneS_4) and closely related acyclic S_4 complexes.[6]

(34) Hinz, F. P.; Margerum, D. W. *Inorg. Chem.* **1974**, *13*, 2941–2949.

(35) (a) Desper, J. M.; Gellman, S. H. *J. Am. Chem. Soc.* **1990**, *112*, 6732–6734. (b) Cooper, S. R.; Rawle, S. C. *Struct. Bonding (Berlin)* **1990**, *72*, 1–72 and references therein. (c) Cooper, S. R. *Acc. Chem. Res.* **1988**, *21*, 141–146.

(36) It should be noted that the observed pH dependence could also be attributed to the reaction involving the protonation/deprotonation of a coordinated hydroxide/water: $Cu^IL(OH) + H^+ \rightleftharpoons Cu^IL(OH_2)^+$. In view of the low pH at which the observed phenomenon occurs, however, reaction 4 would appear to be much more probable. In fact, Kaden and co-workers[11a] have observed pH-dependent behavior for some 12-membered macrocyclic N_2S_2 complexes of Cu(I) which they ascribe to the latter reaction involving ternary hydroxide complexes, but these were observed only at very high pH.

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

Under conditions where eq 9 is valid, a plot of the left-hand term against a_{H^+} should be linear with a slope equal to $K_{H1(Cu^IL)}{}^m$ and an intercept of unity. Such a plot is illustrated for the $Cu^{II/I}$-([15]aneN_2S_3) system in Figure 5 for the pH range 2.3–7.0. Extension of this plot to lower pH values results in a curving off of the slope, presumably due to the fact that the $K_{H1(Cu^{II}L)}a_{H^+}$ term in the denominator of the logarithmic term of eq 8 is becoming appreciable as the system approaches a pH-independent region.

The $K_{H1(Cu^IL)}{}^m$ values obtained by utilizing eq 9 are included in Table III. For the [14]aneNS_3 and [14]aneNSSN systems, where $E_{1/2}$ data were not obtainable at low pH, only a limiting value can be given. Special note should be made of the [14]aneN_2S_2 system, for which application of eq 9 yielded a squared dependence on hydrogen ion activity, rather than a linear plot. This suggests that the $K_{H2(Cu^IL)}{}^m$ term, arising from the formation of a Cu^IH_2L species, is also appreciable for this system (see eq 8), and an excellent quadratic least-squares fit to the data was obtained ($r^2 = 0.999$)—despite a small discontinuity in the data around pH 2.90. However, it is difficult to rationalize the existence of a stable Cu^IH_2L species, since it implies that only the two sulfur donor atoms would remain coordinated to the copper atom. Moreover, no evidence of a corresponding species was observed for the [15]aneN_2S_3 system for which extensive pH data were obtained and for which such a species should be more likely to occur. Our previous studies on Cu^{II}([14]aneN_2S_2) have shown that this complex is unique in that it is extremely slow to dissociate in acidic media,[15] an observation which we have rationalized in terms of the requirement that one of the nitrogens must invert before dissociation can occur, a process that is hindered by high concentrations of hydrogen ion. Since protonation of a nitrogen donor atom in complexes of this ligand requires Cu-N bond rupture accompanied by nitrogen inversion, it is suspected that the experimental data for this system do not represent an equilibrated system insofar as the low-pH data are concerned. Thus, the value of $K_{H2(Cu^IL)}{}^m$ evaluated for the [14]aneN_2S_2 system is deemed highly questionable.

Stability Constants for Cu(I) Complexes. In a recent independent study,[15] the stability constants for the various copper(II)-polyamino polythiaether complexes, defined as

$$K_{Cu^{II}L} = \frac{[Cu^{II}L]}{[Cu_{aq}{}^{2+}][L]} \qquad (10)$$

were determined by means of spectrophotometric measurements.[38] The stability constants for the Cu^IL complexes, K_{Cu^IL}, can be similarly defined as

$$K_{Cu^IL} = \frac{[Cu^IL]}{[Cu_{aq}{}^+][L]} \qquad (11)$$

Substituting eqs 10 and 11 into eq 2 yields the relationship

$$E = E^f - \frac{2.303RT}{n\mathcal{F}} \log \frac{K_{Cu^{II}L}[Cu_{aq}{}^+]}{K_{Cu^IL}[Cu_{aq}{}^{2+}]} \qquad (12)$$

From the corresponding Nernst equation written in terms of the aquated ions, the formal potentials for the $Cu^{II/I}L$ systems, as evaluated at pH > 6.0, correlate to the ratio of the two stability constants as defined in eqs 10 and 11, viz.[6]

$$E^f = E_{aq}{}^{\circ\prime} - \frac{2.303RT}{n\mathcal{F}} \log \frac{K_{Cu^{II}L}}{K_{Cu^IL}} \qquad (13)$$

where $E_{aq}{}^{\circ\prime}$ represents the standard electrode potential, in terms of molar concentrations, for the $Cu_{aq}{}^{2+}/Cu_{aq}{}^+$ redox couple. On the basis of a value of $E_{aq}{}^{\circ\prime} \approx 0.13$ V at 25 °C,[39] the K_{Cu^IL} values for all systems have been calculated and are listed in Table IV.

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

complexed ligand	E^f, V vs NHE	$K_{Cu^IL}'/K_{Cu^{II}L}'$ calcd	$K_{Cu^{II}L}'$ exptl[a]	K_{Cu^IL}' calcd[b]
[14]aneS_4	0.58[c]	$6._0 \times 10^7$	$2.1_8 \times 10^4$	$1. \times 10^{12}$
[14]aneNS_3	0.38	$2._5 \times 10^4$	$1.7_8 \times 10^9$	4×10^{13}
[14]aneN_2S_2	0.04	$4._4 \times 10^{-2}$	$1.8_2 \times 10^{15}$	8×10^{13}
	0.08[d]		7.1×10^{15} [d]	3×10^{13} [d,e]
[14]aneNSSN	−0.01	$6._3 \times 10^{-3}$	$5.2_5 \times 10^{15}$	3×10^{13}
[14]aneN_3S	≤−0.24 (est)		$\geq 10^{20}$	(5×10^{13} assumed)
[14]aneN_4	−0.66[f]		1.6×10^{27} [g]	7×10^{13}
[15]aneS_5	0.68[c]	$2._9 \times 10^9$	$1.5_3 \times 10^4$	4×10^{13}
[15]aneNS_4	0.46	$5._6 \times 10^5$	6.3×10^9	4×10^{15}
[15]aneN_2S_3	0.10	0.46	$1.0_4 \times 10^{16}$	5×10^{15}

[a] Except as noted, all values are from ref 15. [b] All values calculated using eq 13. [c] Reference 6. [d] 20 °C, $\mu = 0.2$; ref 11a. [e] Value for K_{Cu^IL}' extrapolated to aqueous conditions from values determined[11a] directly by potentiometric titration in 2% CH_3CN (log $K_{Cu^IL}' = 9.57$) and in 1% CH_3CN ($K_{Cu^IL}' = 10.35$). [f] Estimated from methanolic potentials of related complexes (see Table III). [g] $\mu = 0.2$: Kodama, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1977**, 1473–1478.

The data in Table IV reveal that, whereas the $Cu^{II}L$ complexes increase in stability by approximately 10^5–10^6 upon the substitution of each amine nitrogen for a thiaether sulfur,[15] the stability constants for the Cu^IL complexes *remain constant* within experimental error as the donor atoms change within each ligand series. The only exception is for those complexes involving ligands containing all thiaether donor atoms (i.e., [14]aneS_4 and [15]aneS_5), where the K_{Cu^IL} values are approximately 40–100 times smaller than those for the corresponding polyamino polythiaethers. Assuming that the K_{Cu^IL} value for Cu^I([14]aneN_3S) is the same as the mean value obtained for the other 14-membered macrocycles containing one or more nitrogen atoms, application of eq 13 permits us to estimate the value of $E_{1/2}$ for this system as well. The resulting estimated potential is included in Tables III and IV. Since the $K_{Cu^{II}L}$ value utilized in making this latter calculation is considered to be a lower limit,[15] the estimated E^f value is correspondingly given as an upper limit.

The constancy of the Cu^IL stability constants is particularly notable in view of the popular conception that sulfur donor atoms stabilize the Cu(I) oxidation state relative to nitrogen donor atoms, a viewpoint commonly stated by both inorganic and biological chemists. The current data clearly demonstrate that the dramatic increase in Cu(II/I) redox potentials observed in macrocyclic ligand complexes with sulfur donor atoms as compared to those with aliphatic nitrogen atoms *is directly attributable to a destabilization of the Cu(II) oxidation state rather than to a stabilization of the Cu(I) oxidation state*. This should have far-reaching implications for our concepts of copper redox chemistry and should influence the future design of ligands for complexing copper.

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[38] As noted in our earlier studies, a perchlorate adduct has been observed to form with the Cu(II)-polythiaether complexes which has the appearance of enhancing the stability of these complexes in solution (Young, I. R.; Ochrymowycz, L. A.; Rorabacher, D. B. *Inorg. Chem.* **1986**, *25*, 2576–2582; cf. ref 32). No investigation of the possibility of such adduct formation has been conducted with the polyamino thiaether complexes. However, since all systems studied have been investigated in 0.10 M ClO_4^-, all results given are internally consistent.

[39] This "concentration potential" value was calculated by correcting the standard potential for the aquocopper(II/I) redox couple ($E^\circ = 0.153$ V: Milazzo, G.; Caroli, S. *Tables of Standard Electrode Potentials*; Wiley: New York, 1978) by the activity coefficients for the aquated ions at an ionic strength of 0.10 M, using the extended Debye–Hückel equation (assuming ionic diameters of 4 Å for each species). Use of the concentration potential rather than the activity potential value alters the calculated ratio of the two stability constants by a factor of 2.

mentation. The diffractometer used in this work was purchased through an equipment grant from the National Science Foundation to Wayne State University.

Registry No. $[Cu([14]aneNS_3)]^{2+}$, 87464-55-9; $[Cu([14]aneN_2S_2)]^{2+}$, 87464-56-0; $[Cu([14]aneNSSN)]^{2+}$, 87464-57-1; $[Cu([14]aneNS_4)]^{2+}$, 116197-98-9; $[Cu([15]aneN_2S_3)]^{2+}$, 137195-80-3; $[Cu([14]aneNS_3)]^{+}$, 87464-71-9; $[Cu([14]aneN_2S_2)]^{+}$, 87464-72-0; $[Cu([14]aneNSSN)]^{+}$, 87464-73-1; $[Cu([14]aneNS_4)]^{+}$, 137167-80-7; $[Cu([15]aneN_2S_3)]^{+}$, 137167-81-8; $[Cu([14]aneS_4)]^{2+}$, 57673-86-6; $[Cu([14]aneS_4)]^{+}$, 93645-98-8; $[Cu([14]aneN_3S)]^{2+}$, 87464-58-2; $[Cu([14]aneN_3S)]^{+}$, 87464-77-5; $[Cu([14]aneN_4)]^{2+}$, 52304-87-7; $[Cu([14]aneN_4)]^{+}$, 88279-82-7; $[Cu([15]aneS_5)]^{2+}$, 60165-93-7; $[Cu([15]aneS_5)]^{+}$, 137167-82-9; $[Cu([14]aneNS_3)]ClO_4$, 137167-83-0; C, 7440-44-0; ClO_4^-, 14797-73-0.

Supplementary Material Available: Tables of thermal parameters, hydrogen parameters, least-squares planes, and torsion angles for $[Cu^I([14]aneNS_3)]ClO_4$ and cyclic voltammetric data for all five copper–polyamino polythiaether complexes studied (23 pages); a listing of calculated and observed structure factors for $[Cu^I([14]aneNS_3)]ClO_4$ (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Isostructural Transition-Metal (Copper, Nickel, Cobalt, and Iron) Compounds with 7,7′,8,8′-Tetracyanoquinodimethanide(1−) in an Unusual Monodentate Coordination Mode. Crystal Structure of Bis(3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole)bis(7,7′,8,8′-tetracyanoquinodimethanido)copper(II)

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The synthesis and properties of compounds $M(abpt)_2(TCNQ)_2$, with M = Cu, Ni, Co, and Fe, abpt = 3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole, and TCNQ = 7,7′,8,8′-tetracyanoquinodimethane, are described. The complexes exhibit very similar spectroscopical and electrical properties. The four compounds appear to be isostructural according to their IR spectra and X-ray powder diffraction data. The crystal structure of $CuC_{48}H_{28}N_{20}$ has been solved. It crystallizes in the triclinic space group, $P\bar{1}$ with $a = 9.194$ (1) Å, $b = 9.761$ (2) Å, $c = 12.235$ (2) Å, $\alpha = 68.29$ (1)°, $\beta = 86.72$ (1)°, $\gamma = 81.80$ (1)°, $V = 1009.7$ (3) Å^3, and $Z = 1$. Heavy-atom techniques were used, and the structure was refined by least-squares methods to a residual R value of 0.052 for 1957 reflections. The copper(II) atom is elongated octahedrally, surrounded by four nitrogens of two symmetry-related abpt ligands (Cu–N = 1.987(5) and 2.046(5) Å) and by two axial, monodentately coordinating $TCNQ^-$ anions (Cu–N = 2.442 (5) Å). The intermolecular TCNQ units form eclipsed dimers, with their mean planes at a close distance of 3.22 Å. At room temperature, all four compounds behave virtually as insulators ($\sigma_{300\,K} = 10^{-7}$–$10^{-10}$ S cm^{-1}).

Introduction

The 3,(4),5-substituted 1,2,4-triazoles have been extensively investigated in our laboratories during the last decade.[2-5] They were studied mainly in combination with various transition-metal salts, because of their tendency to form coordination compounds exhibiting interesting magnetic properties. This kind of ligands can also be used for synthesizing coordination compounds with typically low-dimensional properties, such as electrical conductivity, since the starting materials can be described as *quasi*-square-planar compounds.

In recent years, a number of attempts have been made to obtain so-called molecular metals using more or less square-planar transition-metal chelates that possess one or more paramagnetic centers, in combination with the radical anion $TCNQ^-$, with $TCNQ^-$ = 7,7′,8,8′-tetracyanoquinodimethanide(1−). The copper(II) chelates are of special interest as a donor, because by varying the nature of the ligand the Cu(II)/Cu(I) redox potential of the chelates can be optimized.[6] Therefore, these compounds have the capacity to provide a new type of synthetic metal. Potentially, in these compounds magnetic electrons and conducting electrons can coexist. Examples are the highly conducting compounds of the kind $Cu(phen)_2(TCNQ)_2$ or $Cu(bpy)_2(TCNQ)_2$, with phen = 1,10-phenanthroline and bpy = 2,2′-bipyridine.[7,8] On the other hand, a *semi*conductive or insulating behavior was found in compounds of the formula $Cu_2(PPA)(TCNQ)_3$ or $Cu_2(PPA)(TCNQ)_4$[9] and $Cu_2(L)(TCNQ)_2$,[10] where PPA = 3,6-bis(2-pyridyl)pyridazine and LH_2 is the tetra Schiff base macrocycle resulting from the 2/2 condensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol.

The potentially dinucleating ligand 3,5-bis(pyridin-2-yl)-4-amino-1,2,4-triazole (hereafter abbreviated as abpt, Figure 1) was selected to investigate the conducting, magnetic, and spectroscopic properties of the coordination compounds after combination with the $TCNQ^-$ anion. The results of this study are described below.

Experimental Section

Starting Materials. The ligand abpt was prepared according to the method of Geldard and Lions.[11] The elemental analyses, melting point, and NMR and infrared spectroscopy agreed with the literature data.[11] TCNQ was obtained from Janssen Chemicals. LiTCNQ was prepared by adding a boiling solution of 0.03 mol of LiI in 20 mL of acetonitrile to a boiling solution of 0.01 mol of TCNQ in 200 mL of acetonitrile.

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(2) Keij, F. S.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1984**, 2093.

(3) Prins, R. Forthcoming Ph.D. Thesis, Leiden University, and references therein.

(4) Prins, R.; Birker, P. J. M. W. L.; Haasnoot, J. G.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 4128.

(5) Faulmann, C.; van Koningsbruggen, P. J.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. *Acta Crystallogr., C* **1990**, *C46*, 2357.

(6) Lacroix, P.; Kahn, O.; Valade, L.; Cassoux, P.; Thompson, L. K. *Synth. Met.* **1990**, *39*, 81.

(7) Inoue, M. B.; Inoue, M. *Chem. Phys. Lett.* **1981**, *80*, 585.

(8) Seto, T.; Inoue, M. B.; Inoue, M.; Nakamura, D. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1903.

(9) Wang, W.; Jeng, J. *Synth. Met.* **1988**, *27*, B205.

(10) Lacroix, P.; Kahn, O.; Gleizes, A.; Valade, L.; Cassoux, P. *Nouv. J. Chim.* **1984**, *8*, 643.

(11) Geldard, J. F.; Lions, F. *J. Org. Chem.* **1965**, *30*, 318.

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