

Influence of Coordination Geometry upon Copper(II/I) Redox Potentials. Physical Parameters for Twelve Copper Tripodal Ligand Complexes

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Twelve related tripodal ligands have been synthesized in which the three legs linked to a bridgehead nitrogen are 2-methyl- or 2-ethylthioethyl and/or 2-pyridylethyl or -methyl. Utilization of both terminal methyl and ethyl groups on the thiaether legs was designed to determine whether slight differences in solvation or steric effects might cause detectable changes in properties. Inclusion of both methyl and ethyl linkages of the pyridines to the bridgehead nitrogen provides a comparison of the effect of five- versus six-membered chelate rings, respectively. For each of the tripodal ligands included in this work, the protonation constants and Cu(II) complex stability constants were carefully determined in aqueous solution at 25 °C, $\mu = 0.10$ M (ClO_4^-). The Cu^{II/I}L redox potentials were also determined using slow-scan cyclic voltammetry, thereby permitting the stability of the Cu(I) complexes to be calculated. The stability constants for the twelve Cu(II) complexes range from 10^6 to 10^{17} , increasing by 10^4 – 10^5 as the first and second alkylthioethyl substituents are replaced by 2-pyridylmethyl groups—with only a slight increase upon the introduction of a third pyridyl leg. When 2-pyridylethyl groups are introduced, much smaller trends are noted. For the corresponding Cu(I) complexes, the calculated stability constants are relatively constant (at $\sim 10^{15}$) regardless of the donor set or the length of the pyridyl linkages to the bridgehead. Combination of these data with previous measurements on related macrocyclic and acyclic ligands containing both thiaether sulfur and amine nitrogen donor atoms reveals that, for 35 different uncharged terdentate, quadridentate and quinqueidentate ligands, the stabilities of the Cu^IL complexes lie within the narrow range of about 10^{12} – 10^{16} , with few exceptions, regardless of large differences in coordination geometry and donor strength. For these same 35 ligands, the Cu^{II}L stability constants span 26 orders of magnitude. Thus, the Cu(II/I) potentials, which cover a range of 1.5 V, are shown to be inversely related to the logarithmic values of the Cu^{II}L stability constants for a wide range of ligand types. Future strategies for manipulating the redox behavior of Cu(II/I) systems should recognize that alteration of the ligand coordination geometry primarily impacts the properties of the Cu(II) complex with almost no effect upon the Cu(I) properties.

Introduction

The relationship between redox potentials and both the coordination geometry and the nature of the donor atoms has long been a subject of especial interest in copper chemistry. Vallee and Williams² emphasized the fact that the geometry of the active site in copper redox enzymes should have a direct impact upon their chemical reactivity since Cu(II) tends to prefer six-coordinate tetragonal geometries while Cu(I) predominantly exhibits four-coordinate tetrahedral geometries. They suggested that the (type 1) active site in blue copper proteins might involve an intermediate coordination number of five—a prediction that has, in fact, been corroborated by subsequent crystal structures of azurins and some related blue copper proteins, although four-coordinate trigonal pyramidal geometries are also observed, particularly in plastocyanins.³ The coordination geometries of the copper sites, as well as the nature of the coordinated donor

atoms (typically, one mercaptide sulfur (cysteine), one thiaether sulfur (methionine), and two imidazole nitrogens (histidine)), are generally assumed to stabilize the Cu(I) oxidation state and account for both the high potentials and rapid electron-transfer kinetics exhibited by these proteins.

More than 20 years ago, we conducted a survey⁴ on the redox potentials of a broad series of Cu(II/I) complexes in 80% methanol–20% water (w/w) in which the ligands consisted of nine macrocyclic polythiaethers of varying ring size and eight acyclic compounds containing both thiaether sulfur and amine nitrogen donor atoms. We concluded that high Cu(II/I) potentials could be achieved by sulfur ligation alone without coordinative distortion. At about the same time, Patterson and Holm, reported the results of an even more extensive investigation⁵ in which they determined the potentials of 37 Cu(II/I) complexes in dimethylformamide. Their complexes were selected to demonstrate the effect of both stereochemical and donor atom

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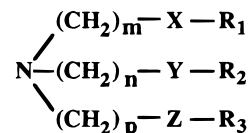
variations on half-wave potentials. Patterson and Holm's results revealed that nonplanar bis-chelate complexes were easier to reduce than their planar analogues; furthermore, rigid planar quadridentate complexes or related planar bis-chelate complexes, differing only in donor atoms, were more readily reduced in the order $N_4 < N_2O_2 < N_2S_2$. From these studies, these authors concluded that the redox potentials parallel the relative ability of the specific ligands to satisfy the coordination preferences of the two copper oxidation states.

More recently, Addison examined a vast array of Cu(II/I) potentials reported in the literature and developed an empirical formula for estimating the potentials based on the structural characteristics of the coordinated ligand.⁶ His correlations also appear to corroborate the concept that Cu(II/I) potential values depend on the degree to which the coordinated ligands accommodate the coordination preferences of Cu(II) or Cu(I). However, none of the foregoing studies has attempted to correlate the redox potentials to the specific stability constants of the Cu(II) and Cu(I) complexes.

The relationship of coordination geometry to potential has a direct bearing on our own recent electron-transfer studies on Cu(II/I) systems since it appears that metastable intermediates of $Cu^{II}L$ and Cu^IL are important in the reaction mechanism.⁷⁻¹² We have suggested⁸ that these metastable species involve distorted geometries which approximate, to at least some extent, the preferred coordination geometry of the opposite oxidation state. Therefore, it is of interest to examine in greater detail how the potential is affected when $Cu^{II}L$ complexes are distorted toward a tetrahedral geometry or Cu^IL species are distorted toward a more planar configuration. The macrocyclic ligands which we have previously examined^{13,14} are representative of the latter situation. In the current work, we have studied the properties of Cu(II/I) systems involving tripodal ligands which are incapable of adapting to a planar geometry but could readily accommodate tetrahedral or distorted tetrahedral geometries. Several of the ligands included in this work are adopted from the work of Karlin and co-workers who have made extensive use of tripodal ligands in following up on their suggestion that the copper sites in many enzymes exhibit geometries which favor Cu(I), presumably as a means of increasing the Cu(II/I) potential.¹⁵

As illustrated below, the most common tripodal ligands are characterized as compounds having three legs, each containing a single donor atom (X, Y, Z), connected to an amine nitrogen by two or three carbon atoms, that is, m , n , and p are usually 2

or 3 to facilitate the formation of five- or six-membered chelate rings:



Many of these ligands have three identical pendant donor atoms ($X = Y = Z$) such as nitrogen (amine,¹⁶⁻²¹ pyridyl,²² quinolyl,²³⁻²⁵ imidazolyl,²⁶ benzimidazolyl,²⁷⁻³³ and pyrazolyl);^{34,35} oxygen (carboxylic³⁶ and alcoholic);³⁷ sulfur (thiaether);³⁸⁻⁴⁰ phosphorus;⁴¹⁻⁴³ or arsenic.⁴¹⁻⁴³ A number of Cu(II/I)-tripodal ligand systems have also been reported in which the donor atoms are not identical on all three legs. Examples include ligands with (i) thiaether sulfurs and pyridyl nitrogens,^{32,44-49} (ii) thiaether sulfurs and benzimidazolyl nitrogens,^{31,44} (iii) pyridyl nitrogens and imidazolyl or benzimidazolyl or quinolyl nitrogens,^{25,44,50,51} (iv) pyridyl or benzimidazolyl nitrogens and alcoholic or carboxylic oxygens,^{31-33,52} and many

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other combinations. Nishida and co-workers are among those who have reported the preparation of ligands with three different legs containing a thiaether sulfur, a pyridyl and a benzimidazolyl group.^{31,44}

For the majority of copper-tripodal ligand studies reported in the literature, the focus has been aimed at structural determinations. In a few cases, Cu(II/I) potentials have also been determined. Measurements of the ligand protonation constants and the stability constants of the copper-tripodal ligand complexes in aqueous solution are primarily limited to tren (tris(2-aminoethyl)amine),^{16–18,53} Me₆tren (tris[2-(dimethylamino)ethyl]amine),²⁰ NTA (nitrilotriacetate),^{54,55} TEA (triethanolamine),^{37,56} and TPMA (tris(2-pyridylmethyl)amine)^{22,57} plus our own recent measurements on TMMEA (tris(methylthioethyl)amine),⁵⁸ all of which have a uniform set of pendant donor atoms. The TPMA and TMMEA class of ligands are of especial interest to Cu(II/I) redox chemistry since both unsaturated nitrogens and thiaether sulfurs have previously been shown to facilitate the reduction of Cu(II) to Cu(I).^{4,59}

Four mixed-donor tripods involving thiaether and pyridyl legs have been previously reported. PMAS⁴⁶ and PEAS,⁴⁵ both of which contain one pyridyl nitrogen and two thioether sulfurs on the pendant legs, were first reported by Karlin, Zubieta and co-workers as purported mimics of the type 1 copper site in blue copper proteins.⁶⁰ As shown in Figure 1, these two ligands (L17b and L18b) differ only in the number of carbons bridging the single pyridine to the bridgehead nitrogen. Nishida and Takahashi have reported briefly on a close analogue of PMAS, namely PMMEA (L17a), and a similar mixed-donor tripodal ligand containing one thiaether sulfur and two 2-pyridylmethyl groups, represented by BPMMEA (L19a) in Figure 1.⁴⁴ However, the protonation constants and the Cu(II) and Cu(I) complex stability constants have not been reported for any of these mixed donor species.

In the current work we have undertaken a systematic study of the Cu(II/I) complexes formed with a series of twelve related tripodal ligands in which the pendant legs contain either thiaether sulfurs or pyridine nitrogens or a mixture of both. For the thiaether legs, both terminal methyl and ethyl groups have been included to determine whether a slight change in the bulkiness of the appended alkyl group has any discernible effect upon the resultant ligand properties. For the pyridyl legs, both methyl and ethyl bridges have been included—in accordance with Karlin and Zubieta's earlier studies—to determine the effect of ring size upon the complex properties. The twelve ligands included in this study are designated as L16a through L22 in Figure 1. [The ligand numbering scheme adopted is contiguous with

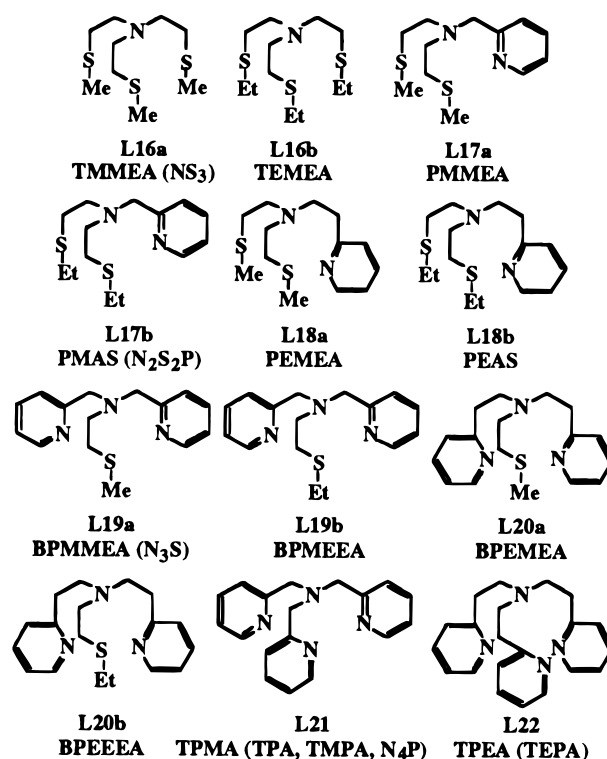


Figure 1. Tripodal ligands included in this work. Alternate ligand designations utilized by some other investigators are shown in parentheses. Numbers assigned to the ligands are arbitrary.

numbers assigned to recently studied macrocyclic¹⁴ and acyclic⁶¹ tetrathiaether ligands.]

The current work includes the determination of (i) the ligand protonation constants, (ii) the Cu(II) complex stability constants, and (iii) the Cu^{II/I} potentials, all of which are reported for aqueous solution at 25 °C, $\mu = 0.10$. From the latter two values, the Cu^IL stability constants are calculated directly. We have previously examined the properties of the symmetric ligands TMMEA (L16a) in aqueous solution and TEMEA (L16b) in 80% methanol⁵⁸ and aqueous data for the symmetric TPMA ligand system (L21) have been reported by previous workers.^{22,57,62} All three systems were re-studied in this work for purposes of comparison. The properties of the other nine ligands are reported here for the first time. In addition, crystal structures are reported for the perchlorate salts of [Cu^I(TMMEA)], [Cu^I(TEMEA)], and [Cu^{II}(TEMEA)Cl].

Experimental Section

General Synthetic Approach. None of the ligands included in this study are known to be commercially available and all were synthesized as part of this work. Synthetic procedures for ligands L16a,⁵⁸ L16b,⁵⁸ L17b,⁴⁶ L18b,⁴⁵ L21,²² and L22⁶³ have been reported in the literature. Ligands L17a and L18a were prepared by adaptation of the methods published for L17b and L18b, respectively, except that bis(2-methylthioethyl)amine⁵⁸ was used in each case instead of bis(2-ethylthioethyl)amine. Ligands L19a and L19b were prepared by the reaction of 1-chloro-2-methylthioethane and 1-chloro-2-ethylthioethane, respectively, with bis(2-pyridylethyl)amine as described below. The latter was

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prepared by reaction of 2-vinylpyridine with ammonium acetate in fashion similar to the preparation of L22.

Our general separation and characterization techniques have been previously described.¹⁴ GC–MS data were obtained for dilute ethanol solutions. Only ¹³C NMR data are reported. While the 400 MHz ¹H NMR spectra are distinguishing, the ¹³C NMR spectra afford a better *a priori* characterization. All solvents employed were EM Scientific reagent grade and all other reagents are from Aldrich Chemical Co.

2-Pyridylmethylbis(2-methylthioethyl)amine (PMMEA = L17a). Under a nitrogen atmosphere, 16.4 g (0.1 mol) of 2-picolyl hydrochloride and 16.5 g (0.1 mol) of bis(2-methylthioethyl)amine⁵⁸ in 250 mL of anhydrous methanol were stirred in the presence of 30.4 g (0.22 mol) powdered potassium carbonate at 40 °C. The progress of the reaction was followed by periodic analysis with GC–MS to completion after 48 h. The crude product mixture was vacuum filtered to remove salts, rotary-vacuum concentrated and Kugelrohr-vacuum distilled three times to afford analytically pure material as a pale yellow oil, bp = 118–122 °C/0.05 Torr, 19.7 g (79.9%). ¹³C NMR (20.15 MHz, CDCl₃), δ in ppm (multiplicity): 15.66 (q), 31.83 (t), 53.61 (t), 60.12 (t), 121.90 (d), 122.83 (d), 136.31 (d), 148.78 (d), 159.61 (s). FT-IR (KBr-neat), $\bar{\nu}$ in cm⁻¹ (relative intensity): 3080 (w), 3005 (w), 2955 (m), 2914 (s), 2830 (m), 1589 (s), 1433 (s), 1113 (s), 756 (s). EI-MS, *m/z* (relative intensity): 256 (0.05), 209 (40), 195 (71), 93 (32), 75 (100). Anal. Calcd for C₁₂H₂₀N₂S₂: C, 56.21; H, 7.86; N, 10.92. Found: C, 56.48; H, 7.60; N, 11.05.

2-Pyridylethylbis(2-methylthioethyl)amine (PEMEA = L18a). The general acid-catalyzed pyridylethylation method of Reich and Levine⁶⁴ was employed. Under a nitrogen atmosphere in 100 mL of absolute methanol were refluxed 21 g (0.2 mol) vinylpyridine, 33 g (0.2 mol) bis(2-methylthioethyl)amine, and 12 g (0.2 mol) glacial acetic acid. After 16 h, GC–MS analysis indicated complete reaction. The reaction mixture was poured into 800 mL of 10% sodium hydroxide and extracted with two 200-mL portions of methylene chloride. The organic phase was dried with MgSO₄, filtered and rotary-vacuum concentrated. The yellow oil residue was Kugelrohr-vacuum distilled three times to isolate analytically pure material as a colorless oil, bp = 120–125 °C/0.05 Torr, 26.3 g (48.7%). ¹³C NMR (100.6 MHz, CDCl₃), δ in ppm (multiplicity): 15.73 (q), 31.90 (t), 36.16 (t), 53.66 (t), 53.89 (t), 121.02 (d), 123.29 (d), 136.07 (d), 149.10 (d), 160.22 (s). FT-IR (KBr-neat), $\bar{\nu}$ in cm⁻¹ (relative intensity): 3080 (w), 3008 (w), 2957 (s), 2914 (s), 2829 (s), 1589 (s), 1474 (s), 1434 (s), 1114 (s), 755 (s). EI-MS, *m/z* (relative intensity): 270 (0.03), 224 (45), 209 (76), 106 (22), 75 (100). Anal. Calcd for C₁₃H₂₂N₂S₂: C, 57.73; H, 8.20; N, 10.36. Found: C, 57.51; H, 8.33; N, 10.10.

Bis(2-pyridylmethyl)-2-methylthioethylamine (BPMMEA = L19a). The precursor bis(2-pyridylmethyl)amine (BPMA) was prepared by the method of Romary et al.⁶⁵ Under a nitrogen atmosphere, 10.2 g (0.051 mol) of BPMA and 7.7 g (0.07 mol) of 1-chloro-2-methylthioethane in 150 mL of dry toluene were stirred at 80 °C. After 3 days, GC–MS analysis showed complete consumption of BPMA and formation of a new major product. The cooled reaction mixture was extracted with 150 mL of 10% HCl and the organic phase discarded. The aqueous phase was adjusted to pH > 9 with 10% NaOH and extracted with two 100-mL portions of methylene chloride. The organic extracts were dried with MgSO₄, filtered, and flash chromatographed on a 4 × 30 cm silica gel column to remove polymeric impurities and recover the desired amine product. The methyl chloride elution concentrate was distilled twice by Kugelrohr fractionation at 115–120 °C/0.05 Torr to afford 7.38 g (53%) of colorless oil product. The oil rapidly darkens unless stored over anhydrous K₂CO₃ at -10 °C. ¹³C NMR (20.15 MHz, CDCl₃), δ in ppm (multiplicity): 15.51 (q), 31.70 (t), 53.21 (t), 60.07 (t), 121.87 (d), 122.84 (d), 136.24 (d), 148.80 (d), 159.35 (s). FT-IR (KBr neat), $\bar{\nu}$ in cm⁻¹ (relative intensity): 3085 (w), 3008 (w), 2915 (m), 1829 (m), 1589 (s), 1569 (m), 1473 (m), 1433 (s), 1363 (w), 1290 (w), 1147 (w), 1147 (w), 1120 (w), 1087 (w), 1047 (w), 995 (m), 760 (s). EI-MS, *m/z* (relative intensity): 273 (1.15), 226 (52), 212 (84), 181 (70), 171 (26), 133 (45), 119 (100), 92 (97), 90 (100), 75 (54), 65

(68), 51 (20). Anal. Calcd for C₁₅H₁₉N₃S: C, 65.90; H, 7.00; N, 15.37. Found: C, 66.11; H, 7.07; N, 15.10.

Bis(2-pyridylmethyl)-2-ethylthioethylamine (BPMEEA = L19b). In identical fashion to the preparation of BPMMEA (L19a), 8.4 g (0.044 mol) of bis(2-pyridylmethyl)amine was reacted with 7.5 g (0.06 mol) of 1-chloro-2-ethylthioethane in 150 mL dry toluene to afford 7.74 g (61%) of pale yellow oil amine product after two Kugelrohr fractionations at 120–140 °C/0.05 Torr. The sample was stored over anhydrous K₂CO₃ at -10 °C to inhibit degradation (as indicated by darkening). ¹³C NMR (20.15 MHz, CDCl₃), δ in ppm (multiplicity): 14.78 (q), 25.94 (t), 29.11 (t), 53.85 (t), 60.21 (t), 121.97 (d), 122.95 (d), 136.38 (d), 148.90 (d), 159.45 (s). FT-IR (KBr-neat), $\bar{\nu}$ in cm⁻¹ (relative intensity): 3083 (w), 3006 (w), 2962 (m), 2925 (s), 2849 (m), 1590 (s), 1569 (m), 1474 (m), 1433 (s), 1364 (m), 1303 (w), 1262 (m), 1148 (m), 1115 (m), 1047 (m), 995 (m), 979 (w), 762 (s). EI-MS, *m/z* (relative intensity): 287 (2.4), 226 (44), 212 (100), 195 (66), 171 (18), 133 (29), 119 (78), 93 (65), 92 (70), 65 (42), 51 (14). Anal. Calcd for C₁₆H₂₁N₃S: C, 66.86; H, 7.36; N, 14.62. Found: C, 67.05; H, 7.49; N, 14.55.

Bis(2-pyridylethyl)amine. In a 1-L flask fitted with a reflux condenser, sealed against the atmosphere with a rubber balloon, was refluxed 105 g (1 mol) vinylpyridine and 38.5 g (0.5 mol) ammonium acetate dissolved in 150 mL of absolute methanol. Periodic analysis of reaction progress by GC–MS showed essentially complete consumption of vinylpyridine after 5 days. The methanol solvent was removed by rotary-vacuum evaporation and the amber colored oil residue was subjected to short-path vacuum distillation at 0.05 Torr. A fraction of 2-pyridylethylamine was recovered at 80–90 °C (16.5%), followed by bis(2-pyridylethyl)amine at 110–120 °C (38%), and, finally, the tris(2-pyridylethyl)amine at 155–180 °C (26%) and undistilled pot residue. The bis(2-pyridylethyl)amine fraction was redistilled by Kugelrohr to afford a colorless NMR pure oil, 41.6 g (36.6%). ¹³C NMR (20.15 MHz, CDCl₃), δ in ppm (multiplicity): 38.88 (t), 49.10 (t), 121.06 (d), 123.30 (d), 1136.17 (d), 149.02 (d), 160.14 (s). EI-MS, *m/z* (relative intensity): 227 (1.1), 135 (100), 121 (14), 106 (80), 93 (44), 78 (26), 65 (11), 51 (9).

1-Chloro-2-methylthioethane and 1-Chloro-2-ethylthioethane. [CAUTION: β-Chlorosulfides are potent vesicant mustards!] On a 0.25 mol scale, 2-mercaptoethanol (stench) was converted under a nitrogen atmosphere to the mercaptide with 1 equiv of potassium hydroxide in 300 mL ethanol. The mercaptide was then reacted with 1 equiv of methyl or ethyl iodide to afford the corresponding 2-alkylthioethanols. Filtration to remove potassium iodide, rotary-vacuum concentration, and Kugelrohr distillation at 50–70 °C/0.03 Torr yielded NMR-pure intermediates in greater than 80% yield. The alcohols were then reacted as 0.5 molar methylene chloride solutions with thionyl chloride to afford the β-chlorosulfides. They were recovered NMR pure by rotary-vacuum evaporation of methylene chloride and Kugelrohr distillation of residues at 40–60 °C/0.05 Torr in greater than 75% yield.

Bis(2-pyridylethyl)-2-methylthioethylamine (BPEMEA = L20a). Under a nitrogen atmosphere 20 g (88 mmol) of bis(2-pyridylethyl)amine and 9.8 g (88 mmol) of 1-chloro-2-methylthioethane was stirred at 50 °C in a suspension of 12.1 g potassium carbonate in 150 mL of toluene. Periodic GC–MS analysis revealed no change in reaction composition after 4 days. The reaction was washed with 500 mL of 5% sodium hydroxide, dried with MgSO₄, filtered, and flash chromatographed on a 4 × 30 cm silica gel column to remove traces of forerun with toluene elution, followed by stripping with methylene chloride to retain polymeric materials and recover the desired amine product. The methylene chloride elution concentrate was Kugelrohr distilled at 160–163 °C/0.05 Torr to afford 16.3 g (61.5%) of colorless oil product. ¹³C NMR (20.15 MHz, CDCl₃), δ in ppm (multiplicity): 15.71 (q), 31.90 (t), 36.15 (t), 53.66 (t), 53.92 (t), 120.97 (d), 123.31 (d), 136.02 (d), 149.09 (d), 160.42 (s). FT-IR (KBr-neat), $\bar{\nu}$ in cm⁻¹ (relative intensity): 3080 (w), 3007 (w), 2957 (m), 2915 (m), 2811 (m), 1590 (s), 1568 (s), 1474 (s), 1434 (s), 1117 (m), 751 (s). EI-MS, *m/z* (relative intensity): 301 (0.06), 254 (83), 240 (76), 209 (21), 161 (13), 147 (36), 135 (55), 106 (100), 93 (18), 75 (47), 51 (9). Anal. Calcd for C₁₇H₂₃N₃S: C, 67.74; H, 7.69; N, 13.94. Found: C, 67.49; H, 7.88; N, 13.80.

(64) Reich, H. E.; Levine, R. *J. Am. Chem. Soc.* **1955**, *77*, 4913–4915.
(65) Romary, J. K.; Barger, J. D.; Bunds, J. E. *Inorg. Chem.* **1968**, *7*, 1142–1145.

Table 1. Crystal Parameters and Experimental Data for X-ray Diffraction Measurements on [Cu^I(TMMEA)]ClO₄, [Cu^I(TEMEA)]ClO₄, and [Cu^{II}(TEMEA)Cl]ClO₄

parameter	[Cu ^I (TMMEA)]ClO ₄	[Cu ^I (TEMEA)]ClO ₄	[Cu ^{II} (TEMEA)Cl]ClO ₄
empirical formula	CuC ₉ H ₂₁ NS ₃ ClO ₄	CuC ₁₂ H ₂₇ NS ₃ ClO ₄	CuC ₁₂ H ₂₇ NS ₃ Cl ₂ O ₄
fw	402.44	444.52	479.97
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>R</i> 3
<i>a</i> , Å	6.562(2)	11.030(2)	10.3609(10)
<i>b</i> , Å	14.401(5)	25.611(4)	10.3609(10)
<i>c</i> , Å	17.439(4)	14.287(2)	16.384(2)
β, deg	90.45(2)	95.06(2)	90
<i>V</i> , Å ³	1647.9(9)	4020.2(11)	1523.2(3)
<i>Z</i>	4	8	3
ρ _{calcd} , g cm ⁻³	1.622	1.469	1.570
μ, mm ⁻¹	1.874	1.544	1.662
<i>R</i> (<i>F</i>) ^b	0.076	0.064	0.049
<i>R</i> _w (<i>F</i> ²) ^c	0.115	0.107	0.111

^a *T* = 295(2) K; λ = 0.710 73 Å. ^b *R*(*F*) = |*F*_c|/Σ|*F*_o| for 2σ(*I*) reflections. ^c *R*_w(*F*²) = [Σ(*F*_o² - *F*_c²)/Σ*w*(*F*_o²)]^{1/2} for 2σ(*I*) reflections.

Bis(2-pyridylethyl)-2-ethylthioethylamine (BPEEEA = L20b). In identical fashion to the preparation of L20a, reaction of bis(2-pyridylethyl)amine with 1-chloro-2-ethylthioethane resulted in isolation of 14.5 g (52.3%) colorless oil product by Kugelrohr distillation at 169–172 °C/0.05 Torr. ¹³C NMR (20.15 MHz, CDCl₃) δ in ppm (multiplicity): 14.90 (q), 26.04 (t), 29.38 (t), 36.16 (t), 53.93 (t), 54.11 (t), 120.95 (d), 123.31 (d), 136.00 (d), 149.08 (d), 160.44 (s). FT-IR (KBr-neat), ν̄ in cm⁻¹ (relative intensity): 3080 (w), 3006 (w), 2960 (m), 2925 (m), 2811 (m), 1591 (s), 1568 (m), 1474 (s), 1434 (s), 1117 (m), 751 (s). EI-MS, *m/z* (relative intensity): 315 (0.02), 254 (51), 240 (60), 223 (16), 147 (34), 135 (50), 106 (100), 89 (49), 78 (25), 61 (19). Anal. Calcd for C₁₈H₂₅N₃S: C, 68.53; H, 7.99; N, 13.32. Found: C, 68.79; H, 8.06; N, 13.05.

Protonation Measurements. All protonation constants were determined from pH titrations. Each titration was carried out in a 200-mL tall-form beaker, immersed in a temperature-controlled jacket, and covered with a rubber stopper into which holes had been bored for the buret, the electrodes and an inlet for nitrogen. Nitrogen gas was continuously swept over the solution to minimize CO₂ absorption. Ionic strength was controlled by the addition of NaNO₃. Prior to the start of each titration, a measured quantity of HClO₄ was added to the solution to ensure that the ligand was completely protonated. This solution was then titrated with a standardized NaOH solution which had been freshly prepared from saturated NaOH to ensure that it was carbonate free. All pH measurements were made using an Orion 901 I analyzer which was standardized daily.

Spectrophotometric Measurements. Scans of the UV–visible spectra were obtained using a Hewlett-Packard model 8452A spectrophotometer. Precise molar absorptivity and stability constant values were measured using a Cary model 17D dual-beam recording spectrophotometer.

Potentiometric Measurements. Formal potentials of all Cu^{II/I}L complexes were determined at ambient temperature in buffered solutions, 0.10 M NaClO₄, using slow-scan cyclic voltammetry with a BAS 100 electrochemical analyzer (Bioanalytical Systems, Lafayette, IN). A typical three-electrode cell was utilized with a glassy carbon working electrode (3 mm dia), a Ag/AgCl reference electrode and a platinum wire auxiliary electrode (all electrodes from BAS). The Ag/AgCl reference electrode contained a 3 M NaCl filling solution (to prevent precipitation of KClO₄ at the junction). The manufacturer reports that the potential for this electrode is 0.208 V.^{66,67} However, extensive measurements in our laboratory with three different Ag/AgCl (3 M NaCl) electrodes applied to six well-characterized redox couples [Fe(phen)₃^{3+/2+}, Ru(NH₃)₃py₃^{3+/2+}, Ru(NH₃)₄bpy₃^{3+/2+}, Ru(NH₃)₂(bpy)₂^{3+/2+}, Co(bpy)₃^{3+/2+}, and ferrocene; phen = 1,10-phenanthroline, py = pyridine, bpy = 2,2'-bipyridine] has shown that the potential of these reference electrodes in aqueous solution is actually 0.226 ± 0.004 V vs SHE.⁶⁶ In view of the uncertainties involved, all potentiometric measurements in this work were made using the aqueous Fe(phen)₃^{3+/2+} (i.e., ferriin) redox couple in an aqueous medium of 0.05 M KCl as an external reference. In correcting our potentials to the standard

hydrogen electrode, the formal potential of the ferriin redox couple in this medium was presumed to be 1.112 V vs SHE.⁶⁸

Results

Structural Determinations. In conjunction with the current investigation, we have determined the crystal structures for the perchlorate salts of [Cu^I(L16a)] (TMMEA) and both [Cu^I(L16b)] and [Cu^{II}(L16b)Cl] (TEMEA). Crystallographic data are listed in Table 1. The bond lengths and bond angles of primary interest are presented in Table 2 along with the corresponding parameters previously determined by Nishida and Takahashi for [Cu^{II}(L16a)Br].⁶⁹ A similar labeling scheme has been adopted for all four structures as shown in the ORTEP drawings representative of the cation units. Figure 2 shows a view of [Cu^{II}(TEMEA)Cl] looking down the virtual 3-fold axis while a side view is presented in Figure 3. In the structures of the TMMEA complexes, atom C(4) is absent, and in both Cu(I) complexes the axial halide atom (X) opposite to the bridgehead nitrogen is missing. Otherwise, the ORTEP drawings for all four compounds are virtually identical.

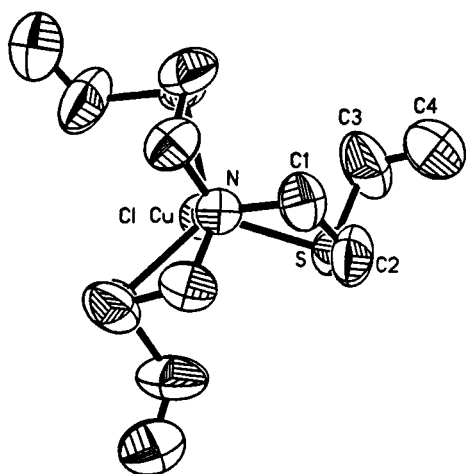
Protonation Constants. The protonation constants for each tripodal ligand were determined from four repetitive titrations of the fully protonated species with freshly prepared carbonate-free NaOH. The individual protonation constants were resolved

- (66) The reported potential for Ag/AgCl electrodes containing saturated KCl is 0.197 V [Bard, A. J.; Faulkner, L. R. *Electrochemical Methods: Fundamentals and Applications*; Wiley: New York, 1980; Figure E.1 (inside back cover)] or 0.1989 V [ref 74, p 335]. An electrode containing 3 M NaCl should be higher in potential, but no literature value is available. Nevertheless, Bates lists the potentials for calomel electrodes filled with saturated KCl and 3 M KCl as 0.2444 and 0.2549 V, respectively [ref 74, p 327]. If a similar 11 mV correction applies to Ag/AgCl electrodes containing 3 M NaCl, the anticipated potential for Ag/AgCl (3 M NaCl) reference electrodes would be about 0.208 V, which agrees with the claim by BAS that these electrodes have a measured potential -0.035 V relative to SCE electrodes (literature values: 0.2412 V [Bard and Faulkner, *op. cit.*] and 0.2444 V [ref 74, p 327]). However, in our independent measurements against six reference redox couples, we found that the miniature SCE electrodes produced by BAS also exhibit abnormally high potentials of 0.262 V. Thus, we agree that the Ag/AgCl (3 M NaCl) electrodes have a potential approximately -35 mV relative to the SCE electrodes produced by BAS, but both types of electrodes appear to give potential readings which are about 18–20 mV too high. These errors are probably attributable to the liquid junction in the miniature electrodes [ref 67]. The use of an external reference system, such as ferriin, eliminates errors arising from the reference electrode potential.
- (67) Howell, J. O. BAS, West Lafayette, IN, personal communication.
- (68) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131–1137. Cf., ref 7.
- (69) Nishida, Y.; Takahashi, K. *Mem. Faculty Sci., Kyushu Univ., Ser. C* **1982**, *13*, 335–342.

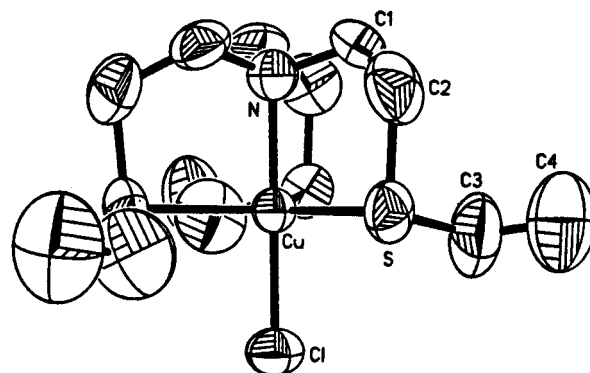
Table 2. Average Crystallographic Bond Lengths and Bond Angles in the Cationic Units of [Cu^I(TMMEA)]ClO₄, [Cu^I(TEMEA)]ClO₄, [Cu^{II}(TMMEA)Br]ClO₄, and [Cu^{II}(TEMEA)Cl]ClO₄

	[Cu ^I (TMMEA)]	[Cu ^I (TEMEA)]	[Cu ^{II} (TMMEA)Br] ^a	[Cu ^{II} (TEMEA)Cl]
		Bond Lengths, Å		
Cu–S	2.26(1)	2.262(6)	2.38(2)	2.366(2)
Cu–N	2.17(1)	2.15(1)	2.08(1)	2.12(2)
Cu–X ^b	—	—	2.409(3)	2.249(5)
N–C(1)	1.48(2)	1.46(1)	1.49(3)	1.48(1)
S–C(2)	1.82(1)	1.80(2)	1.83(4)	1.83(1)
S–C(3)	1.78(2)	1.82(2)	1.83(2)	1.88(1)
C(1)–C(2)	1.54(2)	1.52(1)	1.52(7)	1.50(2)
		Bond Angles, deg		
S–Cu–S	120(2)	120(3)	120(4)	119.8(1)
N–Cu–S	91.2(6)	90.9(5)	87(1)	87.3(1)
N–Cu–X ^b	—	—	178.9(3)	180
S–Cu–X ^b	—	—	93(1)	92.7(1)
Cu–N–C(1)	107.2(9)	107.2(6)	110(1)	108.4(7)
Cu–S–C(2)	94.3(5)	94.2(4)	96(2)	96.9(4)
Cu–S–C(3)	108(2)	109(3)	101(1)	96.9(5)
Cu displacement, Å ^c	–0.046(2)	–0.037(3)	+0.110	+0.111(3)

^a Data taken from ref 69. ^bX = Br or Cl as noted. ^cDisplacement of the Cu atom from the S₃ plane is assigned a negative value if the Cu is on the opposite side of this plane relative to the apical nitrogen and positive if displaced toward the nitrogen.

**Figure 2.** ORTEP drawing showing the structure of the cationic unit for [Cu^I(TMMEA)]ClO₄, [Cu^I(TEMEA)]ClO₄, [Cu^{II}(TMMEA)Br]ClO₄, and [Cu^{II}(TEMEA)Cl]ClO₄ looking down the virtual C_{3v} axis. The same atom numbering scheme is used for all four compounds except that atom C(4) is absent for the TMMEA compounds. For the two Cu(II) compounds, the coordinated halide ion lies underneath the copper atom in this view.

using Martell and Motekaitis' PKAS software⁷² and/or a similar program written in-house,¹³ both of which are based on Bjerrum's \bar{n}_H approach.⁷³ For conversion of activity to molar concentration (and vice-versa), activity coefficients of 0.82 and 0.76 (25 °C, $\mu = 0.10$ M) were used for the aquated hydronium and hydroxide ions as calculated from the extended Debye–Hückel equation using ion size parameters of 9×10^{-8} and 3.5×10^{-8} cm for these two ions, respectively.⁷⁴ The resulting protonation constants for all twelve ligands are given in Table 3 as mixed-mode values, K_{H^m} (i.e., hydronium ion in terms of

**Figure 3.** ORTEP drawing showing the structure of the cationic unit for [Cu^I(TMMEA)]ClO₄, [Cu^I(TEMEA)]ClO₄, [Cu^{II}(TMMEA)Br]ClO₄, and [Cu^{II}(TEMEA)Cl]ClO₄ from a side view. The C(4) atom is absent for the TMMEA compounds, and the halide ion is missing for the two Cu(I) compounds.**Table 3.** Mixed-Mode Protonation Constants Determined for the Tripodal Ligands in Aqueous Solution at 25 °C, $\mu = 0.10$ (NaNO₃)

ligand	log K_{H1}^m	log K_{H2}^m	log K_{H3}^m	log K_{H4}^m
L16a (TMMEA)	8.36(7) ^a			
L16b (TEMEA)	8.32(9)			
L17a (PMMEA)	6.53(6)	<2		
L17b (PMAS)	6.56(8)	<2		
L18a (PEMEA)	7.33(15)	3.26(8)		
L18b (PEAS)	7.35(9)	3.21(6)		
L19a (BPMMEA)	6.29(4)	3.60(3)	<2	
L19b (BPMEEA)	6.23(8)	3.50(4)	<2	
L20a (BPEMEA)	7.66(13)	3.74(3)	2.38(2)	
L20b (BPEEEA)	7.78(7)	3.81(3)	2.58(3)	
L21 (TPMA)	6.24(3)	4.41(2)	2.57(1)	<2
	6.17 ^b	4.35 ^b	2.55 ^b	
L22 (TPEA)	8.21(4)	3.94(3)	3.51(2)	<2

^a A previously reported value of log $K_{H1}^m = 8.22$ was based on a sample found later to contain a small amount of impurities (ref 58).
^b20 °C, $\mu = 0.1$ (ref 22).

activity, all other species in terms of molar concentrations):



(where $n = 1, 2, 3, 4$). In Table 3, entries recorded as log K_{Hn}

(70) McConnell, H.; Davidson, N. *J. Am. Chem. Soc.* **1950**, *72*, 3164–3167. Cf., Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707.

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

(72) Martell, A. E.; Motekaitis, R. J. *Determination and Use of Stability Constants*, 2nd ed.; VCH Publishers: New York, 1992.

(73) Bjerrum, J. *Metal Ammine Formation in Aqueous Solution: Theory of the Reversible Step Reactions*; P. Haase & Son: Copenhagen, 1957.

(74) Bates, R. G. *Determination of pH: Theory and Practice*, 2nd ed.; Wiley: New York, 1973; Table 3-3, p 49.

Table 4. Formal Potential Values for the Copper(II)–Tripodal Ligand Complexes and the Copper(II) and Copper(I) Complex Stability Constants in Aqueous Solution at 25 °C, $\mu = 0.10$ (NaClO₄)

complexed ligand	λ_{\max} , nm ($10^{-3} \epsilon$, M ⁻¹ cm ⁻¹)	E^f (V vs SHE) ^a	log $K_{\text{Cu}^{\text{II}}\text{L}}$	log $K_{\text{Cu}^{\text{I}}\text{L}}$
L16a (TMMEA)	374 (4.76)	0.692	6.29(4) ^b 6.02 ^c	15.80
L16b (TEMEA)	380 (4.73)	0.673	6.35(4) ^b	15.53
L17a (PMMEA)	338 (2.98)	0.384	11.06(3) ^d	15.36
L17b (PMAS)	340 (3.14)	0.397 0.396 ^e	10.48(4) ^d	15.00
L18a (PEMEA)	350 (3.19)	0.595	7.89(4) ^b	15.76
L18b (PEAS)	349 (3.20)	0.607 0.599 ^e	7.87(4) ^b	15.94
L19a (BPMMEA)	254 (11.4)	0.062	16.10(19) ^{f,g}	14.95
L19b (BPMEEA)	255 (10.6)	0.081	15.82(17) ^{f,h}	14.99
L20a (BPEMEA)	340 (3.42)	0.457	9.10(6) ^b	14.63
L20b (BPEEEA)	348 (3.26)	0.471	9.20(3) ^b	14.97
L21 (TPMA)	254 256 (18.30) ^j	-0.147 ⁱ -0.22 ^k	17.59(17) ^g 16.2 ^l	12.9
L22 (TPEA)	260 259 (19.5) ^j	0.51 0.315 ⁿ	9.35(2) ^m	15.8

^a Except as noted, all potentials were experimentally referenced against ferroin as an external standard and corrected to SHE based on a ferroin potential value of $E^f = 1.112$ V (ref 68), see text. ^b Determined using the McConnell–Davidson method at lower pH. ^c Reference 58 (sample may have contained impurities due to degradation). ^d Based on EDTA as a competing ligand using $\log K_{\text{Cu}^{\text{II}}\text{Y}} = 18.78$, $\log K_{\text{H}_1^{\text{m}}} = 10.19$ and $\log K_{\text{H}_2^{\text{m}}} = 6.13$ as representative values for our solutions which contained 0.1 M Na⁺; Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1989; Vol. 6, pp 96, 98. ^e Reference 48. ^f Based on [14]aneN₂S₂ as a competing ligand using a Cu^{II}([14]aneN₂S₂) stability constant value of $\log K_{\text{Cu}^{\text{II}}\text{Z}} = 15.26$ and $\log K_{\text{H}_1^{\text{m}}}$ and $\log K_{\text{H}_2^{\text{m}}}$ values of 9.41 and 5.69; ref 13. ^g Based on [15]aneN₂S₃ as a competing ligand using a Cu^{II}([15]aneN₂S₃) stability constant value of $\log K_{\text{Cu}^{\text{II}}\text{Z}} = 16.02$ and $\log K_{\text{H}_1^{\text{m}}}$ and $\log K_{\text{H}_2^{\text{m}}}$ values of 8.70 and 5.16; ref 13. ^h Based on [14]aneN₂SSN as a competing ligand using a Cu^{II}([14]aneN₂SSN) stability constant value of $\log K_{\text{Cu}^{\text{II}}\text{Z}} = 15.72$ and $\log K_{\text{H}_1^{\text{m}}}$ and $\log K_{\text{H}_2^{\text{m}}}$ values of 9.71 and 6.60; ref 13. ⁱ Baek, H. K.; Holwerda, R. A. *Inorg. Chem.* **1983**, *22*, 3452–3456. ^j Reference 60. ^k Reported as -0.42 V vs Ag/AgCl (for which a value of 0.197 V (vs SHE) was applied in generating the value shown here); ref 62. ^l Reference 57. ^m Based on [14]aneNS₃ as a competing ligand using a Cu^{II}([14]aneNS₃) stability constant value of $\log K_{\text{Cu}^{\text{II}}\text{Z}} = 9.25$ and $\log K_{\text{H}_1^{\text{m}}} = 8.75$; ref 13. ⁿ Baek, H. K.; Karlin, K. D.; Holwerda, R. A. *Inorg. Chem.* **1986**, *25*, 2347–2349.

< 2 could not be resolved from the experimental data. For each entry, the standard deviation is listed in parentheses as the weighted standard deviation of the mean as referenced to the last digits listed (e.g., 8.36(7) and 7.33(15) represent 8.36 ± 0.07 and 7.33 ± 0.15, respectively).

Spectral Parameters. The major absorbance peak in the UV–visible region for each Cu(II) complex included in this work is given in Table 4. For the strongest complexes, the corresponding molar absorptivity values were determined from spectrophotometric mole-ratio plots against Cu(II) using the peak of maximum absorption. For the weaker complexes, the molar absorptivity for the maximum peak was determined simultaneously with the Cu^{II}L stability constant using the McConnell–Davidson method⁷⁰ as previously described.⁷¹ All molar absorptivity values are included in Table 4.

Copper(II) Complex Stability Constants. The stability constants for the Cu(II) complexes with all tripodal ligands included in this study (eq 2) were determined experimentally



as conditional constants, designated by “primed” quantities, since all ligands are subject to protonation:

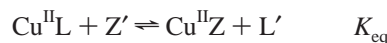
$$K_{\text{Cu}^{\text{II}}\text{L}'} = \frac{[\text{Cu}^{\text{II}}\text{L}]}{[\text{Cu}^{2+}][\text{L}']} = \frac{[\text{Cu}^{\text{II}}\text{L}]}{[\text{Cu}^{2+}]\left(\frac{[\text{L}]}{\alpha_{\text{L}}}\right)} = K_{\text{Cu}^{\text{II}}\text{L}} \alpha_{\text{L}} \quad (3)$$

where α_{L} represents the fraction of the uncomplexed ligand which is in the unprotonated form:

$$\alpha_{\text{L}} = \frac{[\text{L}]}{[\text{L}']} = \frac{[\text{L}]}{[\text{L}] + [\text{HL}^+] + [\text{H}_2\text{L}^{2+}] + [\text{H}_3\text{L}^{3+}]}$$

$$\alpha_{\text{L}} = \frac{1}{1 + K_{\text{H}_1}^{\text{m}} a_{\text{H}^+} + K_{\text{H}_1}^{\text{m}} K_{\text{H}_2}^{\text{m}} (a_{\text{H}^+})^2 + K_{\text{H}_1}^{\text{m}} K_{\text{H}_2}^{\text{m}} K_{\text{H}_3}^{\text{m}} (a_{\text{H}^+})^3} \quad (4)$$

For most Cu(II) complexes, the conditional stability constants were determined by the method of McConnell and Davidson⁷⁰ as previously described.^{71,75} To maintain a constant α_{L} value and to prevent the formation of hydroxycopper(II) species, the solution pH was buffered below 5.5 using our newly developed noncomplexing tertiary amine buffers which have been shown to be unreactive toward aquated Cu(II) ion.⁷⁶ In all cases for which this method was utilized, the conditional stability constants were determined at two different pH values for which $K_{\text{Cu}^{\text{II}}\text{L}'} = 10^3$ – 10^5 . For very strong Cu^{II}L complexes ($K_{\text{Cu}^{\text{II}}\text{L}} > 10^{10}$), a competition method was used in which a second ligand, Z, was introduced into the system:



Under conditions where the total concentration of Cu(II)—designated as C_{Cu} —is less than the sum of the total concentrations of the two ligands (designated as $C_{\text{L}} + C_{\text{Z}}$), the concentration of uncomplexed Cu(II) can be considered negligible for strong complexes.⁷⁷ The value of K_{eq} could then be calculated directly from spectrophotometric measurements of [Cu^{II}L]:

$$K_{\text{eq}} = \frac{K_{\text{Cu}^{\text{II}}\text{Z}'}}{K_{\text{Cu}^{\text{II}}\text{L}'}} = \frac{[\text{Cu}^{\text{II}}\text{Z}][\text{L}']}{[\text{Cu}^{\text{II}}\text{L}][\text{Z}']} = \frac{(C_{\text{Cu}} - [\text{Cu}^{\text{II}}\text{L}]) (C_{\text{L}} - [\text{Cu}^{\text{II}}\text{L}])}{[\text{Cu}^{\text{II}}\text{L}](C_{\text{Z}} - C_{\text{Cu}} + [\text{Cu}^{\text{II}}\text{L}])} \quad (5)$$

In practice, [Cu^{II}L] was measured spectrophotometrically for several solutions containing constant C_{Cu} and C_{L} and varying amounts of C_{Z} . The value of $K_{\text{Cu}^{\text{II}}\text{L}'}$ was then calculated from the mean K_{eq} value and the calculated conditional stability constant for the Cu^{II}Z complex, $K_{\text{Cu}^{\text{II}}\text{Z}'}$, in accordance with eq 5. As competing ligands (Z), EDTA was used for L17a and L17b; [14]aneN₂S₂ and [15]aneN₂S₃ were used for L19a; [14]aneN₂S₂ and [14]aneN₂SSN were used for L19b; [15]aneN₂S₃

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was used for L21; and [14]aneNS₃ was used for L22.⁷⁸ The stability constants and protonation constants utilized for the competing ligands are listed in the footnotes to Table 4. The Cu(II) complexes with L19a, L19b, L21, and L22 do not exhibit absorbance peaks distinct from those of the uncomplexed ligands. For these systems, the absorbances of the Cu^{II}Z species were monitored spectrophotometrically.¹³ The Cu^{II}L stability constant values with all 12 ligands are listed in Table 4. Standard deviations, as listed in parentheses, represent weighted values based on two or more independent determinations.

Formal Potentials and Copper(I) Complex Stability Constants. The formal potentials for all Cu^{II/I}L redox couples were determined in aqueous solution at room temperature (ca. 23 °C) from the half-wave potentials of slow scan cyclic voltammetric measurements ($v \leq 50$ mV s⁻¹) using ferroin as an external reference. The potentials were then corrected relative to SHE as noted in the Experimental Section. On the basis of these potential values and the stability constants determined for the Cu^{II}L complexes, the stability constants for the Cu^IL species were calculated from the following expression:

$$E^f = E_{\text{aq}}^{0'} - \frac{2.303RT}{nF} \log \frac{K_{\text{Cu}^{\text{II}}\text{L}}}{K_{\text{Cu}^{\text{I}}\text{L}}} \quad (6)$$

where $E_{\text{aq}}^{0'}$ represents the concentration potential of the aquated Cu(II/I) redox couple for which a value of $E_{\text{aq}}^{0'} = 0.13$ V was utilized.⁷⁹ The resultant values calculated for $K_{\text{Cu}^{\text{I}}\text{L}}$ are included in Table 4.

Discussion

Structures. In conjunction with the previously reported structure of [Cu^{II}(L16a)Br],⁶⁹ our determination of the structures of [Cu^I(L16a)], [Cu^I(L16b)] and [Cu^{II}(L16b)Cl] demonstrates the close similarities of the corresponding Cu^IL and Cu^{II}L geometries. Both the Cu(I) and Cu(II) complexes have virtual C_{3v} symmetry as illustrated in Figure 2, *the first time that this has been demonstrated for both the Cu(I) and Cu(II) complexes of a redox pair*. In the Cu(I) structures, the axial site trans to the bridgehead nitrogen is completely vacant. Oxidation of Cu(I) to Cu(II) involves the addition of a Cu-X axial bond at this site (Figure 3)—which is presumed to be a Cu-OH₂ bond in aqueous solution. At the same time, as shown in Table 2, the Cu-N bond shortens by 0.03–0.09 Å and the three Cu-S bonds lengthen by 0.11–0.12 Å as the copper is oxidized. This is consistent with the known preference of Cu(II) for amine nitrogen relative to thiaether sulfurs whereas Cu(I) shows no such preference.¹³ Although the Cu atom remains nearly coplanar with the S₃ plane in both oxidation states, it does move slightly through this plane due to the shortening of the Cu(II)-N bond—that is, the Cu(II) atom is slightly above the S₃ plane while the Cu(I) atom is slightly below this plane, relative to the position of the apical nitrogen. Otherwise, all changes in bond angles are of a minimal nature and there are no remarkable features to these structures despite the C_{3v} symmetry.

A survey of known Cu(I) and Cu(II) complex structures in the Cambridge database ($R < 0.08$) shows that the copper-nitrogen bond lengths in our compounds are within normal distances for both oxidation states: 2.16(9) for Cu^I-NR₃ (101

structures) and 2.08(9) for Cu^{II}-NR₃ (815 structures). The Cu^{II}-SR₂ bond lengths are also within the normal range (2.42(14) Å for 187 structures) but the Cu^I-SR₂ bonds appear to be on the short end relative to the majority of known compounds (2.33(9) Å for 112 structures).

The observations made above are reasonably consistent with the observed crystal structures reported by Karlin and co-workers for [Cu^I(L17b)]⁴⁶ and [Cu^{II}(L17b)SO₄],⁴⁶ the only other tripodal ligand system—among those included in this work—which involves only five-membered chelate rings and for which both Cu^IL and Cu^{II}L structures are available. Although the C_{3v} symmetry is lost for this redox couple—with one S-Cu-N(pyridine) angle significantly smaller than the other in both oxidation states—the trends in bond length changes are similar, though exaggerated. In [Cu^I(L17b)], the Cu-N(amine) and Cu-S bond lengths are virtually identical to those found in our Cu(I) compounds. However, upon oxidation to Cu(II), the former bond shortens by an even greater extent (0.13 Å) and the two Cu-S bonds lengthen by 0.18 Å while the Cu-N(pyridine) bond length remains nearly constant.

Crystallographic structural determinations of several of the other cationic complexes included in this work have also been previously reported including [Cu^{II}(L17a)I];⁴⁴ [Cu^I(L18b)];⁴⁵ [Cu^{II}(L18b)NO₃];⁸⁰ [Cu^{II}(L19a)Br];⁴⁴ [Cu^{II}(L19a)N₃];⁴⁴ at least seven [Cu^{II}(L21)X] complexes in which X represents benzoylformate,⁸¹ Br,⁸² Cl,¹⁵ F,⁸³ NO₂,⁸⁴ ONO,^{84,85} and H₂O;⁶² [Cu^I(L22)];⁶³ and at least seven [Cu^{II}(L22)X] complexes in which X represents Br,⁸² Cl,¹⁵ ONO,⁸⁶ NO₃,⁸⁷ methylimidazole,⁶³ acetate,⁸⁸ and H₂O.⁸⁸ For those systems containing one or more six-membered chelate rings, the virtual C_{3v} symmetry is destroyed and, in the Cu(II) complexes in particular, the coordination sphere more nearly approximates a square pyramidal geometry with the donor atom of one of the six-membered chelate rings occupying the axial site.¹⁵

Based on all known structures of copper complexes with tripodal ligands, the Cu(II/I) redox pairs with TMMEA and TEMEA (L16a and L16b) appear to exhibit the smallest structural differences, the addition of the fifth (axial) ligand upon oxidation to Cu(II) being the most prominent feature. This implies that the contribution of the reorganizational barrier to the electron-transfer kinetics may be abnormally small, a possibility which is currently being explored in our laboratory.

Protonation Constant Trends. For all tripodal ligands included in this work, the bridgehead amine nitrogen is the most basic donor atom present. Therefore, the first K_{H} value might be anticipated to be relatively constant for all ligands, although internal hydrogen bonding (through a bridging water molecule) to a pyridine donor atom might be anticipated to increase the first K_{H} value for all ligands other than L16a and L16b. However, the substitution of one pyridine for a thiaether sulfur

(78) [14]aneN₂S₂ = 1,4-dithia-8,11-diazacyclotetradecane; [14]aneNSSN = 1,11-dithia-4,8-diazacyclotetradecane; [15]aneN₂S₃ = 1,4,7-trithia-10,13-diazacyclotetradecane; [14]aneNS₃ = 1,4,8-trithia-11-azacyclotetradecane.

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results in a marked lowering of the $\log K_{\text{HI}}$ value. This decrease is most evident for the 2-pyridylmethyl compounds for which the $\log K_{\text{HI}}^{\text{m}}$ value remains depressed as a second and third pyridine are added. For the 2-pyridylethyl compounds, the initial decrease is less severe and the $\log K_{\text{HI}}^{\text{m}}$ value then increases as a second and third pyridine are substituted. These trends do not lend themselves to a simple rational explanation but indicate that solvation effects are very important in amine protonation as has been previously noted for simple tertiary alkylamines.^{89–91} With the exception of L17a and L17b, the K_{H2}^{m} values, representing protonation of a pyridine nitrogen, are relatively uniform for the entire series of ligands. This is consistent with the observations of Arnett et al.⁹² that the apparent basicity of pyridine nitrogens in solution is primarily a function of the substituent effects, which are uniform in our ligands.

Stability Constant and Redox Potential Trends. For the current set of tripodal ligand complexes, a 10^4 – 10^5 -fold enhancement in the $K_{\text{Cu}^{\text{II}}\text{L}}$ value is observed for the substitution of a 2-pyridylmethyl moiety in place of each of the first two alkylthioethyl groups—presumably reflecting the strong preference of Cu(II) for unsaturated nitrogens compared to thiaether sulfurs. Substitution of a third 2-pyridylmethyl group causes only a minor increase in the $\text{Cu}^{\text{II}}\text{L}$ stability, presumably because the fourth donor atom is forced to occupy an axial site which is normally elongated in Cu(II) complexes due to Jahn–Teller distortion since the C_{3v} symmetry is lost. For the ligands containing 2-pyridylethyl legs, the stability enhancement for each of the first two pyridyl substitutions amounts to only one and one-half orders of magnitude as a result of the decreased stability of six-membered chelate rings. Substitution of the third 2-pyridylethyl leg for the remaining alkylthioethyl group causes no change in the $\text{Cu}^{\text{II}}\text{L}$ stability.

The stability constant values for the Cu(I) complexes formed with all tripodal ligands included in this work are relatively constant, the majority having values of approximately 10^{15} . At the same time, the Cu(II) complexes exhibit stabilities which range over more than eleven orders of magnitude (10^6 – $10^{17.5}$). We also note that the $\text{Cu}^{\text{I}}\text{L}$ stability constants are very similar to the values previously calculated (i) for macrocycles with N_xS_{4-x} and N_xS_{5-x} donor sets, (ii) for S_4 macrocycles with variable cavity size and (iii) for corresponding acyclic S_4 ligand complexes—as determined in previous studies conducted within our laboratory.^{13,61,71,79,93} The relative uniformity in the stability of the $\text{Cu}^{\text{I}}\text{L}$ complexes means that the redox potentials are almost wholly dependent upon the stabilities of the $\text{Cu}^{\text{II}}\text{L}$ complexes.

The foregoing conclusion is dramatically illustrated in Figure 4 where the E^{f} values for 35 copper complex systems—included in the current and previous studies—are seen to parallel almost exactly the $\log K_{\text{Cu}^{\text{II}}\text{L}}$ values. All of the ligands represented in this figure are multidentate species and all but one ($[\text{9}]\text{janeS}_3$)⁹⁴ contain at least four donor atoms. Only ligands which are unchanged in their unprotonated form are included in order to

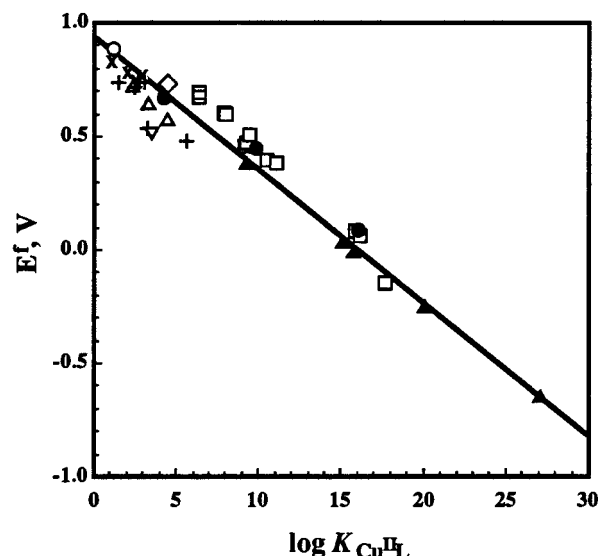


Figure 4. Plot of the formal potentials for 35 $\text{Cu}^{\text{II}}\text{L}$ redox couples as a function of the logarithmic values of the $\text{Cu}^{\text{II}}\text{L}$ stability constants. Open squares represent tripodal ligands included in this work. Solid triangles and circles represent, respectively, macrocyclic quadridentate and quinquadentate ligands containing a mixture of thiaether sulfur and amine nitrogen donor atoms. Open triangles represent macrocyclic S_4 ligands of variable ring size (13–16-membered rings) while the crosses represent corresponding ligands with substituted $-\text{OH}$ groups (or, in the case of $[\text{12}] \text{janeS}_4$, a fused oxathiane ring). The open circle represents $[\text{21}] \text{janeS}_6$; the diamond represents $[\text{9}] \text{janeS}_3$ (the 1:1 complex); and the X's represent acyclic tetrathiaether complexes. The line drawn has the Nernstian slope of 0.059 V and represents an “average” value of $\log K_{\text{Cu}^{\text{II}}\text{L}} = 13.8$. (Data for individual points are listed in Table S1, Supporting Information.)

eliminate electrostatic effects. Otherwise, the ligands represent a wide variety of types containing variable donor atoms (thiaether sulfurs, amine nitrogens, and pyridyl nitrogens) and variable structures including macrocycles (of varying ring size and donor number), open chain (acyclic) and tripodal structures. (Specific data for the points represented in Figure 4 are listed in Table S1 of the Supporting Information.)

The line drawn in Figure 4, which passes through the systems with the highest and lowest E^{f} values, has the Nernstian slope of 0.059 and represents an “average” $\log K_{\text{Cu}^{\text{II}}\text{L}}$ value of 13.8. It is to be noted that the $K_{\text{Cu}^{\text{II}}\text{L}}$ values cover a range of 26 orders of magnitude and the Cu(II/I) potentials range over 1.5 V. Since complexes with $K_{\text{Cu}^{\text{II}}\text{L}} < 10$ cannot be forced to form completely under reasonable solution conditions, we infer that the practical upper limit for Cu(II/I) systems may be close to that represented in Figure 4 by $\text{Cu}^{\text{II}}([\text{21}] \text{janeS}_6)$ (open circle) for which $E^{\text{f}} = 0.89$ V.⁹⁵ The lowest Cu(II/I) potentials obtainable are limited only by the maximum stability constants which can be generated for Cu(II) complexes—although it may be difficult to exceed the -0.66 V represented in Figure 4 for $\text{Cu}^{\text{II}}([\text{14}] \text{janeN}_4)$ ($[\text{14}] \text{janeN}_4 = \text{cyclam}$).⁷⁹

As a group, the redox couples involving tripodal ligands (open square symbols in Figure 4) lie slightly above the dominant line since their $\text{Cu}^{\text{I}}\text{L}$ complexes are 1.2–1.9 log units more stable than the “average” value of $\log K_{\text{Cu}^{\text{I}}\text{L}} = 13.8$. (The lone exception is TPMA for which the potential value may be in error.) Although this indicates that the tripodal ligands do result in a slight stabilization of the $\text{Cu}^{\text{I}}\text{L}$ species, this is relatively insignificant compared to the general observation that varying

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(i) the nature of the donor atoms, (ii) the number of donor atoms, (iii) the chelate ring size, (iv) the macrocyclic ring size, and (v) the general ligand morphology have an almost negligible impact on $K_{\text{Cu}^{\text{II}}\text{L}}$ values. By contrast, the stability of the $\text{Cu}^{\text{II}}\text{L}$ complexes is drastically affected by all of these parameters.

In view of the constraints imposed by macrocyclic structures on the ligand flexibility, it is not surprising that the macrocyclic S_4 ligand systems (open triangles and crosses) in Figure 4 lie below the line although the deviation is relatively small. However, it is surprising that there is little distinction between the $\text{Cu}^{\text{II}}\text{L}$ stabilities as the macrocyclic ring size increases or as one progresses to acyclic S_4 ligands (X 's). Moreover, previous statements (including those by us) that sulfur donor atoms tend to stabilize $\text{Cu}(\text{I})$ relative to amine nitrogen donor atoms are completely incorrect as shown by both the tripodal ligands and the macrocyclic ligands involving variable donor atoms (solid triangles and circles).

The relative invariance of the $\text{Cu}(\text{I})$ complex stability constants has been noted earlier for several limited series of ligands^{14,61,79,96,97} but has not previously been recognized to exist on a broader scale. As noted above, the ligands represented in Figure 4 include amine nitrogen, pyridine nitrogen and thiaether sulfur donor atoms and the various ligands exhibit definitive preferences for planar or tetrahedral coordination geometries. Thus, we conclude that, due to its d^{10} electronic configuration, $\text{Cu}(\text{I})$ exhibits little preference for one type of donor over the other or for five- vs six-membered chelate rings; nor is it strongly influenced by constraints in the coordination geometry, even when a copper-ligand donor atom is forced to rupture upon reduction as is believed to occur with copper complexes involving [12]- and [13]ane S_4 macrocycles.^{93,96,98} The preference of $\text{Cu}(\text{I})$ for tetrahedral coordination, as exhibited in the crystal structures, is attributed to repulsive forces.⁹⁹ Therefore, it is

largely misleading to state that any specific ligand "stabilizes" the $\text{Cu}(\text{I})$ oxidation state to a significant extent.

Conclusion

The data plotted in Figure 4 imply that attempts to alter the thermodynamics of $\text{Cu}(\text{II}/\text{I})$ electron transfer should focus on the manipulation of the structure and composition of the coordination sphere in terms of its impact upon the $\text{Cu}^{\text{II}}\text{L}$ complexes since *the complex stabilities of the $\text{Cu}^{\text{II}}\text{L}$ complexes appear to be relatively impervious to the influence of donor atom or structural alterations* in aqueous solution. Thus, the earlier trends in $\text{Cu}(\text{II}/\text{I})$ potentials noted by Patterson and Holm⁵ and by Addison⁶ as a function of ligand structure merely reflect the effects on the $\text{Cu}(\text{II})$ complex stabilities. This conclusion has significant implications in terms of the prevailing theories about the influence of distorted geometries upon the electron-transfer properties of redox-active biological copper sites. It would also appear to play an important role in the kinetics of low molecular weight $\text{Cu}(\text{II}/\text{I})$ systems insofar as the kinetic behavior is dependent upon the relative stabilities of metastable $\text{Cu}^{\text{II}}\text{L}$ and $\text{Cu}^{\text{I}}\text{L}$ intermediates which influence the preferred reaction pathway in the dual-pathway square scheme mechanism observed in many $\text{Cu}(\text{II}/\text{I})$ redox systems as studied in our laboratory.⁷⁻¹² The small impact of distorted geometries upon the stability of $\text{Cu}(\text{I})$ complexes may account to a large extent for our observation that, *in the $\text{Cu}(\text{II}/\text{I})$ electron-transfer reactions observed to date, the preferred pathway has tended to involve a distorted $\text{Cu}^{\text{I}}\text{L}$ intermediate rather than a distorted $\text{Cu}^{\text{II}}\text{L}$ species.*

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-9528831.

Supporting Information Available: X-ray crystallographic files, in CIF format, for $[\text{Cu}^{\text{I}}(\text{TMMEA})]\text{ClO}_4$, $[\text{Cu}^{\text{I}}(\text{TEMEA})]\text{ClO}_4$ and $[\text{Cu}^{\text{II}}(\text{TEMEA})\text{Cl}]\text{ClO}_4$ and a table listing the potentials and $\text{Cu}^{\text{II}}\text{L}$ and $\text{Cu}^{\text{I}}\text{L}$ stability constants for all thirty-five $\text{Cu}^{\text{II}}\text{L}$ systems included in Figure 4 are also available free of charge via the Internet at <http://pubs.acs.org>.

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