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Copper(II) Complexes of N_2S_3 Ligands Involving Aromatic Nitrogen and Thioether Donors and Having High Redox Potentials

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The new ligands 1,9-bis(3,5-dimethyl-1-pyrazolyl)-2,5,8-trithianonane (L1) and 1,9-bis(benzimidazolyl)-2,5,8-trithianonane (L2) and their Cu(II) complexes as the BF_4^-, ClO_4^-, and $CF_3SO_3^-$ salts have been prepared. The X-ray structures of $[Cu(L1)][BF_4]_2$ and $[Cu(L3)][CF_3SO_3]_2$ (L3 = 1,9-bis(2-pyridyl)-2,5,8-trithianonane) have been determined. Crystal data for monoclinic $[Cu(L1)][BF_4]_2$: space group $C2/c$ (No. 15); $a = 20.84(1)$ Å, $b = 18.74(4)$ Å, $c = 14.980(9)$ Å; $\beta = 120.00(3)°$; $Z = 8$; $R = 0.041$, $R_w = 0.073$ for 2641 reflections. Crystal data for monoclinic $[Cu(L3)][CF_3SO_3]_2$: space group $P2_1/c$ (No. 14); $a = 12.217(5)$ Å, $b = 14.636(4)$ Å, $c = 15.102(3)$ Å; $\beta = 97.87(2)°$; $Z = 4$; $R = 0.077$, $R_w = 0.061$ for 1600 reflections. The electronic and ESR spectra and cyclic voltammetry of the new complexes have been determined and are discussed in terms of their structures in both solid and solution. Evidence is presented for subtle but significant steric influences on the kinetics and thermodynamics of Cu(II)/Cu(I) redox and upon the electronic structures of the Cu centers.

Introduction

Investigation of low molecular weight models of the active sites in "blue" copper proteins has revealed much about the coordination chemistry of that element. For example, influences of coordination geometry, donor atom identity and number have been explored extensively for tetradentate ligands containing aromatic nitrogen and thioether sulfur donors similar to those in the "blue" copper protein N_2S_2 systems.[1–5] In addition to these comprehensive examinations of tetradentate ligands, less exhaustive evaluations of cyclic S_n and S_xN_{n-x} ($n = 3$–8; $x = 1$–n) systems[6–13] have also been conducted. It is of interest to compare the results from these cyclic systems with those from acyclic analogs, such as, for example, the pentadentate N_2S_3 system. Unfortunately, acyclic pentadentate N_2S_3 ligands have been less thoroughly studied,[4,11,14] and information about their coordinating properties, electrochemistry of their complexes, and general reactivity is relatively limited. We have recently described such a system[15] and this report deals with an extension of that work that has revealed, among other things, a high redox potential for a Cu(II)/Cu(I) couple.

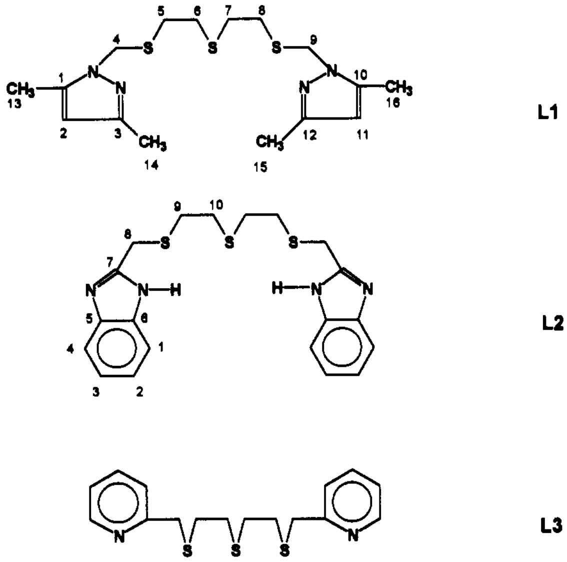

Figure 1. Ligands with position identification.

Experimental Section

Commercially available reagents were obtained from the Aldrich Chemical Co., Inc., or from Morton Thiokol Alfa Products Inc. and were used without further purification. Those used for cyclic voltammetry measurements were spectroscopic grade. We have previously described preparations for 1,9-bis(2-pyridyl)-2,5,8-trithianonane (ligand L3) and its complex $[Cu(L3)][CF_3SO_3]_2$.[15] Spectroscopic data were obtained by using the following instruments: IR, Mattson Polaris FT; UV/vis, Cary Model 17; ESR, Bruker ESP-300 X-band spectrometer operating at ~9.5 GHz. Solution "glasses" for ESR measurements were prepared by plunging sealed capillaries containing ~10^{-4} mol/L solutions into liquid nitrogen. Magnetic susceptibility data were obtained at room temperature by the Faraday method. Electrochemical measurements were carried out under a nitrogen atmosphere at room temperature by using a Cypress Systems, Inc., CS-1087 computer-controlled potentiostat. Solution concentrations were 10^{-3} mol/L in complex and 0.1 mol/L in supporting electrolyte (tetraethylammonium perchlorate). Voltammograms were recorded in acetonitrile by using a glassy-carbon working electrode that was prepolished with 0.3 μm Al_2O_3, a platinum counterelectrode, and an aqueous saturated calomel reference electrode checked periodically relative

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to a 1.0×10^{-3} mol/L solution of ferrocene in acetonitrile containing 0.1 mol/L tetraethylammonium perchlorate for which the ferrocene/ferrocenium reduction potential was 400 mV. The reference electrode was separated from the bulk of the solution by a porous Vycor tube. Junction potential corrections were not used. Voltages reported versus the normal hydrogen electrode were obtained by adding 244 mV to the potential measured versus SCE. X-ray diffraction data were collected by using a Rigaku AFC6S diffractometer. Analyses were performed by Canadian Microanalytical Service Ltd.

Preparative Details. 1-(Chloromethyl)-3,5-dimethylpyrazole. In a three-neck round-bottom flask, 1-(hydroxymethyl)-3,5-dimethylpyrazole[16] (12.6 g, 0.100 mol) was dissolved in dry dichloromethane (60 mL) at 0 °C. To this chilled solution was added thionyl chloride (11.9 g, 7.30 mL, 0.100 mol) dropwise. The temperature of the mixture was not allowed to exceed 5 °C, and stirring was continued for 1 h. Volatiles were removed, and the residue was washed with dry diethyl ether before being dried *in vacuo*: yield 12 g (83%); mp 110–111 °C. NMR ($CDCl_3$, ppm from TMS internal standard): ^{1}H, 6.18 (s, 3H, –CH$_2$– + C–H), 2.40 (s, 3H, CH$_3$), 2.33 (s, 3H, CH$_3$); ^{13}C, 147 (C*–Me), 146 (C*–Me), 108.7 (–C*H–), 52.28 (–C*H$_2$–), 11.16 (C*H$_3$), 10.62 (C*H$_3$).

1,9-Bis(3,5-dimethyl-1-pyrazolyl)-2,5,8-trithianonane (Ligand L1). 1-(Chloromethyl)-3,5-dimethylpyrazole (14.4 g, 10.0 mmol) was dissolved in dry dimethylformamide (30 mL), and 2-mercaptoethyl sulfide (7.7 g, 5.0 mmol) dissolved in dry dimethylformamide (10 mL) was added slowly. The reaction mixture was then heated to 90–100 °C for approximately 20 min after which a solution of KOH (6.7 g, 12 mmol) in water (20 mL) was added dropwise with continued heating. Heating was then stopped, and water (100 mL) was added. The reaction mixture was cooled and extracted with dichloromethane (3 × 35 mL). The extracts were dried over anhydrous Na_2SO_4 and volatiles were removed. The solid residue was washed with diethyl ether: yield 10 g (54%); mp 55 °C. NMR ($CDCl_3$, in ppm from TMS internal standard, position identification from Figure 1): ^{1}H, 5.84 (s, 2H, C2 C11), 5.11 (s, 4H, C4 C9), 2.82 (m, 4H, C5 C8), 2.65 (m, 4H, C6 C7), 2.29 (s, 6H, C14 C15), 2.18 (s, 6H, C13 C16); ^{13}C, 147.49 (C3 C10), 138.84 (C1 C12), 106.48 (C2 C11), 49.57 (C4 C9), 31.63, 30.98 (C5-C8), 13.32 (C14 C15), 10.99 (C13 C16).

1,9-Bis(1-benzimidazolyl)-2,5,8-trithianonane (Ligand L2). This ligand was prepared in a manner analogous to that described above: yield 80%; mp 75 °C. NMR ($CDCl_3$, in ppm from TMS internal standard, assignments from heteronuclear and homonuclear COSY, position identification from Figure 1): ^{1}H, 10.64 (s, 1H, NH), 7.56 (m, 2H, ArH), 7.21 (m, 2H, ArH), 4.07 (s, 4H, –CH$_2$–), 2.5 (m, 8H, –CH$_2$–CH$_2$–); ^{13}C, 152.0 (C5), 138.0 (C6), 123.12 (C7), 123.04 (C1 C4), 115.0 (C2 C3), 32.0 (C8), 31.5 (C10), 29.0 (C9).

Complexes. Preparation for all complexes were similar to that for [Cu(L1)][ClO$_4$]$_2$.

[Cu(L1)][ClO$_4$]$_2$. A solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.37 g, 1.00 mmol) in methanol (30 mL) was added to a solution of 1,9-bis(3,5-dimethyl-1-pyrazolyl)-2,5,8-trithianonane (0.37 g, 1.00 mmol) in methanol (20 mL) and stirred for 20 min. After filtration, a green crystalline compound was obtained by slow evaporation of the filtrate: yield 0.38 g (60%); mp 165 °C dec. FAB–mass spectrum: calcd for $[C_{16}H_{26}N_4S_3Cu]^+$ and $[C_{16}H_{26}N_4S_3]^+$, *m/e* = 432 and 370; found, *m/e* = 432 and 370. Anal. Calcd for $C_{16}H_{26}Cl_2CuN_4O_8S_3$: C, 30.35; H, 4.11; N, 8.85. Found: C, 30.10; H, 4.19; N, 8.59.

[Cu(L1)][BF$_4$]$_2$: yield 55%; mp 260 °C dec.

[Cu(L1)][CF$_3$SO$_3$]$_2$: yield 50%; mp 250 °C dec.

[Cu(L2)][ClO$_4$)$_2$: yield 75%; mp 180 °C dec. FAB–mass spectrum: calcd for $[C_{20}H_{22}N_4S_3Cu]^+$ and $[C_{20}H_{22}N_4S_3]^+$, *m/e* = 477 and 414; found, *m/e* = 477 and 414..

[Cu(L2)][BF$_4$]$_2$: yield 70%; mp 165 °C dec. Anal. Calcd for $C_{20}H_{22}B_2CuF_8N_4S_3$: C, 36.84; H, 3.38; N, 8.59. Found: C, 36.67; H, 3.60; N, 8.64.

[Cu(L2)][CF$_3$SO$_3$]$_2$: yield 65%; mp 150 °C dec. FAB–mass spectrum: calcd for $[C_{20}H_{22}N_4S_3Cu]^+$ and $[C_{20}H_{22}N_4S_3]^+$, *m/e* = 477 and 414; found, *m/e* = 477 and 414.

X-ray Studies. A summary of crystal data for [Cu(L1)][BF$_4$]$_2$ and [Cu(L3)][CF$_3$SO$_3$]$_2$ is in Table 1. Diffraction intensities were collected at 298 K by using the ω-2θ scan technique to a maximum 2θ value of 50.0° for [Cu(L1)][BF$_4$]$_2$ and 120.2° for [Cu(L3)][CF$_3$SO$_3$]$_2$. Three standards measured after every 150 reflections showed no indication of significant crystal decay. The space group was determined by systematic absences, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structures. Unit cell parameters (Table 1) were determined by a least-squares refinement of the setting angles of 23 reflections ($20.41° < 2\theta < 27.08°$) for [Cu(L1)][BF$_4$]$_2$ and 25 reflections ($48.65° < 2\theta < 49.92°$) for [Cu(L3)][CF$_3SO_3$]$_2$. Lorentz and polarization factors were applied and corrections were made for absorption. The structure was solved by direct methods[17,18] and refined by full-matrix least-squares methods[19] with counting statistics weights. Non-hydrogen atoms were refined anisotropically for [Cu(L1)][BF$_4$]$_2$ and anisotropically or isotropically for [Cu(L3)][CF$_3$SO$_3$]$_2$. H-atom positions were calculated, but their parameters were not refined. The final cycle of refinement for [Cu(L1)][BF$_4$]$_2$ was based on 2641 observed reflections ($I > 3.00\sigma(I)$) and 320 variables and converged while that for [Cu(L3)][CF$_3$SO$_3$]$_2$ was based on 1600 observed reflections ($I > 3.00\sigma(I)$) and 278 variables and converged. All calculations were performed with the TEXSAN[20] crystallographic software of Molecular Structure Corp., and scattering factors were from the usual source.[21]

Table 1. Crystallographic Data[a]

complex	[Cu(L1)][BF$_4$]$_2$	[Cu(L3)][CF$_3$SO$_3$]$_2$
chem formula	$C_{16}H_{26}B_2CuF_8N_4S_3$	$C_{18}H_{20}CuF_6N_2O_6S_5$
fw	607.74	698.20
space group	*C*2/*c* (No. 15)	*P*2$_1$/*c* (No. 14)
a (Å)	20.84(1)	12.217(5)
b (Å)	18.740(4)	14.636(4)
c (Å)	14.980(9)	15.102(3)
β (deg)	120.00(3)	97.87(2)
T (°C)	25	25
μ (cm^{-1})	11.71	54.89
ρ_{calcd} (g cm^{-3})	1.594	1.734
V (Å^3)	5066(9)	2675(1)
Z	8	4
λ (Å)	0.71069	1.54178
R[b]	0.041	0.077
R_w[c]	0.036	0.061

[a] Estimated standard deviations for data in this table and elsewhere in this paper refer to the least significant figure and are given in parentheses. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

Results

Herein, we report synthesis of the acyclic pentadentate N_2S_3 donor ligands 1,9-bis(3,5-dimethyl-1-pyrazolyl)-2,5,8-trithianonane (ligand L1) and 1,9-bis(benzimidazolyl)-2,5,8-trithianonane (ligand L2) and their Cu(II) complex cations as the ClO_4^-, BF_4^-, and $CF_3SO_3^-$ salts. We also report the X-ray structures of the new complex [Cu(L1)][BF$_4$]$_2$ and, for comparison, that of previously reported[15] [Cu(L3)][CF$_3$SO$_3$]$_2$. The results of the X-ray structural studies of [Cu(L1)][BF$_4$]$_2$ and [Cu(L3)][CF$_3$SO$_3$]$_2$ are given in Figures 2 and 3 and in Tables 1–5. One of the BF_4^- anions was found to be disordered and was treated as having eight fluorines, each with half-occupancy. Both $CF_3SO_3^-$ anions were disordered. One involved a simple CF_3 rotation while the other was treated as being in two separate orientations with occupancy 0.6 and 0.4. The new ligands were prepared by condensation of 2-mercaptoethyl sulfide and 1-(chloromethyl)-3,5-dimethylpyrazole (L1) or 1-(chloromethyl)benzimidazole (L2). Complexes of these ligands were obtained by reactions between them and an equimolar amount of the appropriate copper salt in methanol. All are soluble in common solvents like methanol, acetonitrile, and *N*,*N*-dimethylformamide. Electronic spectra of these complexes are summarized in Table 6. All exhibit two broad bands with λ_{max} in the ranges 860–910 and 575-640 nm. ESR spectral data are given in Table 6. Powdered samples and

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(19) Function minimized: $\sum w(F_o - F_c)^2$, where $w = 4F_o^2/\sigma^2(F_o)^2$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, and Lp = Lorentz–polarization factor.

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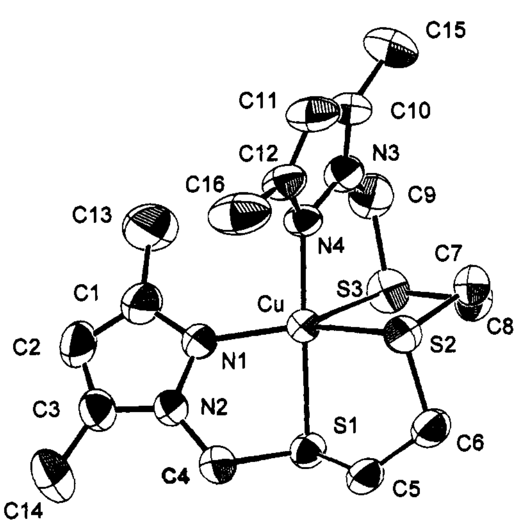

Figure 2. X-ray structure of $[Cu(L1)]^{2+}$.

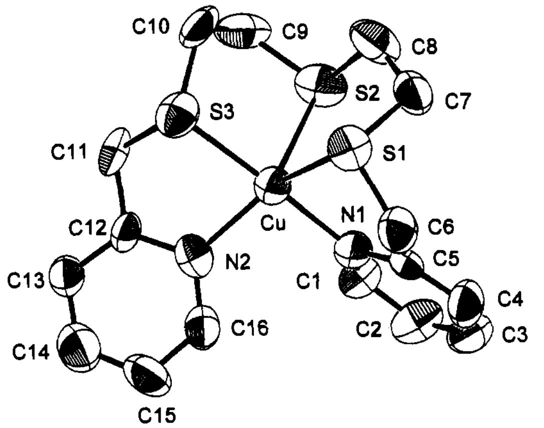

Figure 3. X-ray structure of $[Cu(L3)]^{2+}$.

solutions give different spectra in most cases suggesting structural changes are occurring during the dissolving process as we have noted in previous reports on related systems.[15,22] Electrochemical data are given in Table 7. Most of the electrode processes are quasi-reversible although in a few cases, values of ΔE_p and i_{pa}/i_{pc} approach those for reversible character. The redox potentials of $[Cu(L1)]^{2+}$ as its BF_4^-, ClO_4^-, or $CF_3SO_3^-$ salts are notable for their high positive values of 928–954 mV vs NHE.

Discussion

Preparations of the ligands are unremarkable as are syntheses of the Cu(II) complex salts. The single-crystal X-ray structural study of $[Cu(L1)][BF_4]_2$ reveals a distorted square pyramidal N_2S_3 coordination geometry about copper (Figure 2 and Table 4). The largest deviation from ideal geometry in this cation involves displacement of N1 toward S2 to give a reduced bond angle N(1)–Cu–S(2) = 149.0(1)° and an enlarged bond angle N(1)–Cu–S(3) = 120.0(1)° whereas angles of 180 and 90° are expected. The basal Cu–S distances of 2.320(2) and 2.342(2) Å are comparable to those in similar structures such as that formed by 1,9-bis(2-thienyl)-5-oxa-2,8-dithianonane (2.353(2) Å) or 1,6-bis(2-thienyl)-2,5-dithiahexane (2.368(1) Å).[22] The somewhat elongated apical Cu–S bond (2.502(2) Å) can be compared to analogous bonds in the complexes of 1,9-bis(2-pyridyl)-2,5,8-trithianonane (2.472(5) Å) (*vide infra*) or 1,4,7,10,13-pentathiacyclopentadecane (2.398(2) Å) which show similar lengthening.[15,23]

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors for $[Cu(L1)][BF_4]_2$

atom	*x*	*y*	*z*	B_{eq}[a] (Å^2)
Cu(1)	0.13350(4)	0.23602(3)	0.11648(5)	3.33(3)
S(1)	0.17793(8)	0.11997(7)	0.1406(1)	3.65(6)
S(2)	0.08097(8)	0.20835(7)	0.2186(1)	3.78(6)
S(3)	0.24184(8)	0.29350(8)	0.2672(1)	4.56(7)
F(1)	0.9464(2)	0.0565(2)	0.0817(2)	5.7(2)
F(2)	0.8602(2)	0.0619(2)	–0.0872(2)	6.1(2)
F(3)	0.8794(2)	0.1568(2)	0.0152(3)	6.2(2)
F(4)	0.9654(2)	0.1265(2)	–0.0253(3)	6.8(2)
F(5A)	0.7605	–0.0066	0.5547	9.8(6)
F(5B)	0.7494	–0.0301	0.4842	13.5(9)
F(6A)	0.6424	0.0053	0.5116	8.9(6)
F(6B)	0.6340	–0.0138	0.4514	10.4(7)
F(7A)	0.7068	–0.0885	0.6030	10.2(6)
F(7B)	0.7275	–0.0100	0.6127	14.0(8)
F(8A)	0.6754	–0.0790	0.4383	13.2(8)
F(8B)	0.6944	–0.1131	0.5286	10.1(5)
N(1)	0.1325(3)	0.2254(2)	–0.0164(3)	4.4(2)
N(2)	0.1257(2)	0.1579(2)	–0.0539(3)	3.8(2)
N(3)	0.1273(3)	0.3866(2)	0.1643(3)	4.0(2)
N(4)	0.0906(3)	0.3323(2)	0.0972(3)	3.6(2)
C(1)	0.1319(4)	0.2672(3)	–0.0884(5)	5.9(3)
C(2)	0.1225(4)	0.2268(4)	–0.1709(5)	6.3(3)
C(3)	0.1181(3)	0.1576(3)	–0.1480(4)	4.8(3)
C(4)	0.1258(3)	0.0969(3)	0.0051(4)	4.3(3)
C(5)	0.1234(3)	0.0763(3)	0.1899(4)	4.2(3)
C(6)	0.1212(3)	0.1216(3)	0.2711(4)	4.5(3)
C(7)	0.1344(3)	0.2675(3)	0.3269(4)	4.7(3)
C(8)	0.2174(3)	0.2739(3)	0.3637(4)	5.0(3)
C(9)	0.2076(4)	0.3824(3)	0.2308(5)	5.6(3)
C(10)	0.0817(4)	0.4414(3)	0.1526(5)	5.1(3)
C(11)	0.0136(4)	0.4213(3)	0.0775(5)	5.9(3)
C(12)	0.0201(3)	0.3545(3)	0.0447(4)	4.6(3)
C(13)	0.1443(6)	0.3473(4)	–0.0732(7)	11.0(5)
C(14)	0.1065(4)	0.0906(4)	–0.2081(5)	7.9(4)
C(15)	0.1099(5)	0.5087(3)	0.2150(6)	8.4(4)
C(16)	–0.0392(4)	0.3098(3)	–0.0370(6)	7.6(4)
B(1)	0.9125(4)	0.1007(4)	–0.0046(5)	4.2(3)
B(2)	0.6994(5)	–0.0422(5)	0.5220(7)	5.6(4)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

The X-ray structure of $[Cu(L3)][CF_3SO_3]_2$ (Figure 3 and Table 5) reveals a distorted square pyramidal N_2S_3 coordination sphere about copper in this compound as well. The basal Cu–S bonds (2.413(5) and 2.300(5) Å) show greater variation in length than those in $[Cu(L1)][BF_4]_2$ (*vide supra*) or even those in the same cation as its perchlorate salt[15] (2.324(5) and 2.360(5) Å) although in that compound there is close approach by a perchlorate oxygen to hydrogens in one pyridine ring which influences bond angles in the cation and may also thereby indirectly affect bond lengths. The apical Cu–S distance (2.472(5) Å) in $[Cu(L3)][CF_3SO_3]_2$ is comparable to that in the perchlorate salt (2.454(4) Å).[15] In fact, differences between the cation's structure when isolated as the perchlorate and as the triflate salt are minor as might be anticipated with the greatest difference in bond lengths being 0.053 Å at Cu–S(1) and the greatest difference in bond angle being 5.0° at S(2)–Cu–N(2) in the triflate salt. In spite of these differences being rather small, they have a striking influence on the electronic structure of the copper atom, which is immediately apparent upon visual inspection of the two salts. Samples of the perchlorate are deep blue whereas those of the triflate are bright green! This difference can be appreciated more precisely from electronic and ESR spectra of the salts as we have previously reported.[15]

As in the perchlorate salt, there is no bonding contact between anion and copper in the triflate salt where the shortest anion-copper distance is 3.266(2) Å (Cu–O(4B)). There is, however, a short van der Waals contact of 2.500 Å between an oxygen atom (O(2)) in a triflate ion lying under the base plane of the square pyramid and the C(1) hydrogen atom's calculated position. This contact presumably has structural and other consequences like those previously reported for the perchlorate[15] and is at least

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Table 3. Positional Parameters and Equivalent Isotropic Temperature Factors for $[Cu(L3)][CF_3SO_3]_2$

atom	*x*	*y*	*z*	$B_{eq}{}^a$ (Å^2)
Cu(1)	0.6720(2)	0.4451(2)	0.8303(1)	4.4(1)
S(1)	0.6286(4)	0.5741(3)	0.7322(3)	5.5(2)
S(2)	0.5856(4)	0.3472(3)	0.7068(3)	5.9(3)
S(3)	0.5059(3)	0.4448(3)	0.8860(3)	5.4(2)
N(1)	0.818(1)	0.449(1)	0.7859(8)	4.7(7)
N(2)	0.733(1)	0.4142(8)	0.9577(8)	4.4(7)
C(1)	0.885(1)	0.375(1)	0.791(1)	6(1)
C(2)	0.984(2)	0.376(1)	0.758(1)	6(1)
C(3)	1.012(1)	0.452(2)	0.716(1)	7(1)
C(4)	0.945(2)	0.527(1)	0.706(1)	6(1)
C(5)	0.851(1)	0.522(1)	0.743(1)	5(1)
C(6)	0.771(1)	0.605(1)	0.737(1)	6(1)
C(7)	0.607(1)	0.512(1)	0.625(1)	6(1)
C(8)	0.532(2)	0.435(1)	0.627(1)	7(1)
C(9)	0.467(1)	0.310(1)	0.753(1)	7(1)
C(10)	0.410(1)	0.385(1)	0.802(1)	7(1)
C(11)	0.546(1)	0.356(1)	0.970(1)	4.3(8)
C(12)	0.665(1)	0.378(1)	1.013(1)	3.8(8)
C(13)	0.695(1)	0.362(1)	1.101(1)	4.7(9)
C(14)	0.802(2)	0.381(1)	1.136(1)	7(1)
C(15)	0.876(2)	0.414(1)	1.084(1)	7(1)
C(16)	0.837(2)	0.430(1)	0.996(1)	6(1)
S(4)	0.2989(4)	0.6315(3)	0.6158(3)	5.3(2)
F(1A)	0.168(2)	0.693(1)	0.476(1)	6.8(5)
F(1B)	0.108(3)	0.557(2)	0.530(2)	9.2(8)
F(2A)	0.182(2)	0.539(1)	0.494(1)	8.4(5)
F(2B)	0.109(6)	0.692(5)	0.544(5)	25(2)
F(3A)	0.096(2)	0.636(2)	0.585(1)	9.0(6)
F(3B)	0.199(3)	0.641(3)	0.452(2)	12(1)
O(1)	0.291(1)	0.5551(8)	0.6735(8)	7.4(7)
O(2)	0.291(1)	0.7169(9)	0.653(1)	10(1)
O(3)	0.388(1)	0.627(1)	0.5623(8)	9.1(8)
C(17)	0.173(2)	0.615(2)	0.529(2)	9.2(7)
S(5A)	0.2156	0.3212	1.0055	6.9
O(4A)	0.1065	0.3548	1.0263	8.1
O(5A)	0.2306	0.2975	0.9139	9.9
O(6A)	0.3210	0.3414	1.0723	7.7
S(5B)	0.2614	0.2845	1.0124	9.3
O(4B)	0.2841	0.3686	1.0511	7.2
O(5B)	0.1831	0.3408	0.9227	15.7
O(6B)	0.3315	0.2186	0.9751	14.6
C(18A)	0.207(1)	0.1963(8)	1.0430(8)	44.2(3)
F(4A)	0.124(1)	0.150(1)	0.9998(9)	8.4(3)
F(5A)	0.300(1)	0.161(2)	1.026(1)	14.1(3)
F(6A)	0.202(1)	0.192(1)	1.1290(7)	7.8(3)
C(18B)	0.156(2)	0.238(2)	1.031(2)	22(1)
F(4B)	0.108(4)	0.209(3)	0.953(2)	22(1)
F(5B)	0.220(3)	0.174(3)	1.070(3)	22(1)
F(6B)	0.081(3)	0.259(3)	1.082(3)	22(1)

[a] B_{eq} is the mean of the principal axes of the thermal ellipsoid.

Table 4. Selected Bond Lengths and Angles in $[Cu(L1)][BF_4]_2$

	Distances (Å)		
Cu-S(1)	2.320(2)	Cu-N(1)	1.990(4)
Cu-S(2)	2.342(2)	Cu-N(4)	1.970(4)
Cu-S(3)	2.502(2)		
	Angles (deg)		
S(1)-Cu-S(2)	88.34(5)	S(2)-Cu-N(1)	149.0(1)
S(1)-Cu-S(3)	98.82(6)	S(2)-Cu-N(4)	88.4(1)
S(1)-Cu-N(1)	82.3(1)	S(3)-Cu-N(1)	120.0(1)
S(1)-Cu-N(4)	176.4(1)	S(3)-Cu-N(4)	82.9(1)
S(2)-Cu-S(3)	90.64(7)	N(1)-Cu-N(4)	99.6(2)

partly responsible for the close similarity between the geometry of the coordination spheres of the cation in the two salts.

Powdered samples of $[Cu(L1)]^{2+}$ as the ClO_4^-, BF_4^-, or $CF_3SO_3^-$ salts show only isotropic ESR spectra (Table 6) as do the BF_4^- and $CF_3SO_3^-$ salts of $[Cu(L2)]^{2+}$. On the other hand, $[Cu(L2)][ClO_4]_2$ has a spectrum compatible with rhombic distortion of a square pyramidal cation, and all three salts of $[Cu(L3)]^{2+}$ have spectra consistent with the distorted square pyramidal structures revealed by X-ray studies on $[Cu(L3)][CF_3SO_3]_2$ (this work) or $[Cu(L3)][ClO_4]_2$.[15] The frozen *N,N*-dimethylformamide solution "glass" spectra at 77 K (Table 6) are axial in all cases. It is significant that the green color of solid $[Cu(L3)][CF_3SO_3]_2$ is replaced by a deep blue color when it is dissolved in any of a variety of weakly coordinating solvents. This has been observed previously and has been interpreted to indicate interaction in solution between copper and an oxygen atom of $CF_3SO_3^-$.[15] In fact, the ESR, cyclic voltammetric, and electronic spectroscopic evidence suggests that anion interaction in the sixth coordination site is a general phenomenon in all but strongly coordinating solvents.[15,22] For example, the fact that all ESR spectra of DMF solution glasses at 77 K are axial and show no rhombic splitting suggests that structure change must have accompanied dissolving, at least in those cases where the solid-state spectra indicate rhombic distortions. This change may be induced by solvation or by interaction with the anion in the open or sixth coordination site. In solvents of low coordinating ability, such as dichloromethane or acetonitrile, as we have shown in earlier work,[15] the interaction is usually with the anion, but in more nucleophilic solvents, such as *N,N*-dimethylformamide, there is a dissociative equilibrium involving the ligand during which the associated anion is also replaced by solvent.[15,22] In the present work, dissociation is also observed in "glass" ESR spectra and is revealed as a superpositioning of the spectra of two species. One is a solvate of the appropriate cupric salt and the other is the complex. It seems likely, therefore, that the structural changes upon dissolving are similar to those described above.

Table 5. Selected Bond Lengths and Angles in $[Cu(L3)][CF_3SO_3]_2$

	Distances (Å)		
Cu-S(1)	2.413(5)	Cu-N(1)	1.99(1)
Cu-S(2)	2.472(5)	Cu-N(2)	2.02(1)
Cu-S(3)	2.300(5)		
	Angles (deg)		
S(1)-Cu-S(2)	87.4(2)	N(1)-Cu-N(2)	95.7(5)
S(1)-Cu-S(3)	95.5(2)	S(3)-Cu-N(2)	83.0(4)
S(1)-Cu-N(1)	84.5(4)	S(3)-Cu-N(1)	177.8(4)
S(1)-Cu-N(2)	141.5(4)	S(2)-Cu-N(2)	130.8(4)
S(2)-Cu-S(3)	88.2(2)	S(2)-Cu-N(1)	94.0(4)

The electronic spectra (Table 6) show d–d bands typical for square pyramidal or octahedral species[24] in all cases. As expected,[15,24] the d–d bands near 625 nm show a slight anion dependence in acetonitrile or nitromethane but no dependence on these solvents. In fact, the spectral characteristics are dominated by influences from the organic ligand and the greatest effect is obtained through changes in that ligand rather than in weak solvation or anation.

Cyclic voltammetry (Table 7), like ESR spectroscopy, is a more sensitive probe than electronic spectroscopy of the interaction of anions and solvent in the sixth coordination site on copper. The cyclic voltammograms we have obtained are typical of quasi-reversible processes. Values of ΔE_p vary from 80 to 184 mV, but the ratio i_{pc}/i_{pa} in each case remains nearly equal to 1 at all reasonable scan rates. Values of $E_{1/2}$ for the perchlorate and triflate salts, both of which in acetonitrile solution seem to have anions interacting with copper through their oxygen atoms, are similar for each of the three cations but differ slightly from those of their tetrafluoroborate salts where any interaction with copper would have to be through a fluorine atom.

Although the cyclic voltammograms thus provide support for the proposed solution structures of these species, their most interesting aspect involves the variation of $E_{1/2}$ and ΔE_p with ligand. It is strikingly apparent that all three salts of $[Cu(L1)]^{2+}$ have values of $E_{1/2}$ that lie in the range 928–954 mV vs NHE whereas salts of $[Cu(L2)]^{2+}$ and $[Cu(L3)]^{2+}$ have values that lie ~200 mV lower in the range 718–742 mV vs NHE. The higher of these values, as exhibited by $[Cu(L1)]^{2+}$, are of interest since

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Table 6. Electronic and ESR Spectroscopic Data

complex	λ_{max} (nm) (ϵ (L mol^{-1} cm^{-1}))^a			ESR	
				powder	solution^b
$[Cu(L1)][ClO_4]_2$	900 (125)	650 (300)	350 (sh)	$g_i = 2.074$	$g_o = 2.094^c$ $\lvert A_o\rvert = 69 \times 10^{-4\ d}$
$[Cu(L1)][CF_3SO_3]_2$	900 (100)	650 (250)	350 (sh)	$g_i = 2.066$	$g_\parallel = 2.404$ $g_\perp = 2.064$ $\lvert A_\parallel\rvert = 140 \times 10^{-4}$
$[Cu(L1)][BF_4]_2$	905 (70)	650 (200)	345 (sh)	$g_i = 2.063$	$g_\parallel = 2.414$ $g_\perp = 2.070$ $\lvert A_\parallel\rvert = 140 \times 10^{-4}$
$[Cu(L2)][ClO_4]_2$	860 (100)	640 (150)	400 (sh)	$g_1 = 2.204$ $g_2 = 2.106$ $g_3 = 2.008$	$g_\parallel = 2.306$ $g_\perp = 2.037$ $\lvert A_\parallel\rvert = 146 \times 10^{-4}$
$[Cu(L2)][CF_3SO_3]_2$	860 (100)	640 (150)	400 (sh)	$g_i = 2.108$	$g_\parallel = 2.314$ $g_\perp = 2.045$ $\lvert A_\parallel\rvert = 146 \times 10^{-4}$
$[Cu(L2)][BF]_4$	860 (125)	650 (140)	400 (sh)	$g_i = 2.110$	$g_\parallel = 2.310$ $g_\perp = 2.069$ $\lvert A_\parallel\rvert = 143 \times 10^{-4}$
$[Cu(L3)][ClO_4]_2$	915 (200)	600 (400)	350 (5800)	$g_1 = 2.04$ $g_2 = 2.06$ $g_3 = 2.14$	$g_\parallel = 2.36$ $g_\perp = 2.06$ $\lvert A_\parallel\rvert = 152 \times 10^{-4}$
$[Cu(L3)][CF_3SO_3]_2$	915 (200)	600 (400)	350 (5800)	$g_1 = 2.02$ $g_2 = 2.08$ $g_3 = 2.16$	$g_\parallel = 2.36$ $g_\perp = 2.05$ $\lvert A_\parallel\rvert = 152 \times 10^{-4}$
$[Cu(L3)][BF_4]_2$	900 (150)	580 (550)	340 (3400)	$g_1 = 2.05$ $g_2 = 2.06$ $g_3 = 2.14$	$g_\parallel = 2.37$ $g_\perp = 2.05$ $\lvert A_\parallel\rvert = 149 \times 10^{-4}$

^{a} In CH_3CN, CH_3OH or CH_3NO_2. ^{b} In $HCON(CH_3)_2$ at 77 K unless otherwise specified. ^{c} At 294K; suitable "glass" at 77 K unobtainable. ^{d} In cm^{-1}.

Table 7. Cyclic Voltammetric Data

complex	$E_{1/2}$ (mV vs NHE)	ΔE_p (mV)^a
$[Cu(L1)][ClO_4]_2$	954	184
$[Cu(L1)][CF_3SO_3]_2$	948	97
$[Cu(L1)][BF_4]_2$	928	117
$[Cu(L2)][ClO_4]_2$	718	172
$[Cu(L2)][CF_3SO_3]_2$	726	143
$[Cu(L2)][BF_4]_2$	743	153
$[Cu(L3)][ClO_4]_2$	734	80
$[Cu(L3)][CF_3SO_3]_2$	729	88
$[Cu(L3)][BF_4]_2$	729	97

^{a} Scan rate 100 mV/s.

they are among some of the larger such values known. Other high values recently reported are 1.08 V for $[Cu(Et_2S_5)]^{2+}$ (Et_2S_5 = 3,6,9,12,15-pentathiaheptadecane),[25] 0.999 V for $[Cu(bddo)]^{2+}$ (bddo = 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane),[4] and 1.15 V vs NHE for $[Cu(Qdto)]^{2+}$ (Qdto = 1,8-bis(2′-quinolyl)-3,6-dithiaoctane).[14] However, unlike the ligands in these studies which provide S_5, N_2S_2, and N_2S_2 coordination spheres, respectively, all three ligands in the present report are N_2S_3 donors with two aromatic nitrogens and three thioether sulfurs separated by similar carbon bridges. It is of interest, therefore, to explain the differences in redox potentials exhibited by our three complex cations.

There are significant variations particularly with respect to Cu–S bond lengths in the coordination sphere of $[Cu(L1)][BF_4]_2$ compared to $[Cu(L3)][CF_3SO_3]_2$ or $[Cu(L3)][ClO_4]_2$[15] and other square pyramidal copper complexes in general. In $[Cu(L1)][BF_4]_2$, there is one *long* Cu–S distance of 2.502(2) Å to a sulfur *adjacent* to the aromatic ring and two Cu–S distances to more remote sulfurs that are shorter at 2.320(2) and 2.342(2) Å. In $[Cu(L3)]^{2+}$, whether as the ClO_4^- or $CF_3SO_3^-$ salt, the pattern of Cu–S distances involves two relatively *short* distances of 2.324(5) and 2.360(5) Å to both sulfurs *adjacent* to the aromatic rings and a longer bond of 2.454(4) Å to the more remote sulfur (perchlorate salt[15]) or 2.413(5), 2.300(5), and 2.472(5) Å (triflate salt) (Table 5) which is more typical of such complexes.[15] It is clear that one Cu–S bond in $[Cu(L1)]^{2+}$ is significantly weaker than other Cu–S bonds in the same cation or than bonds to *comparably located* sulfur donors in ligands in square pyramidal copper complexes in general.

Furthermore, the values of ΔE_p for $[Cu(L1)]^{2+}$ salts are much larger than those for either $[Cu(L2)]^{2+}$ or $[Cu(L3)]^{2+}$ salts (Table 7) which suggests greater structural rearrangement is occurring during redox activity by $[Cu(L1)]^{2+}$ salts. Thus, it seems that rupturing the weakest Cu–S bond in each of the complexes in order to achieve a tetrahedral Cu(I) reduction product is kinetically more difficult but thermodynamically more favorable in the $[Cu(L1)]^{2+}$ structure than in cases involving sulfur donors located differently in their ligands such as those found in the $[Cu(L2)]^{2+}$, $[Cu(L3)]^{2+}$, and most other square pyramidal thioether complex salts of copper. In other words, steric demands by a ligand (in this case, presumably by the methyl groups of L1) outside the primary coordination sphere appear to have serious impact on the placement of a ligand's donors within the coordination sphere, and this in turn has an unexpectedly profound influence on the kinetics and thermodynamics of redox. Furthermore, this effect is not necessarily achieved by merely increasing the size of the terminal groups on the ligand chain as can be seen from the fact that L2 with a benzimidazolyl group behaves more like L3 with analogously placed pyridyl groups than does L1 with its methyl-substituted pyrazolyl units.

It is of significance that Addison has recently reported similar observations[14] with respect to the influence of methyl groups α to coordinated pyridine nitrogens of an N_2S_3 ligand, Mptn = 1,9-bis(6′-methyl-2′-pyridyl)-2,5,8-trithianonane. Their presence raised $E_{1/2}$ for $[Cu(Mptn)]^{2+}$ by about 200 mV (to 0.945 V vs NHE) compared to the unmethylated analogue. This number corresponds closely to the value we have observed in the present study with our methylated pyrazolyl ligand. As part of Addison's explanation of the influence of the methyl group in his pyridyl systems, he proposed, on the basis of computerized molecular modeling, an altered mode of coordination by the ligand. His proposed mode is precisely that found in our X-ray study of $[Cu(L1)][BF_4]_2$ involving an α-methylated pyrazolyl ligand which causes comparable change in $E_{1/2}$.

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Conclusions

The electronic structure of Cu(II) is extremely sensitive to even apparently minor changes in bond lengths (<0.06 Å) and bond angles (<5°) as indicated by the dramatic changes in color and electronic and ESR spectra of $[Cu(L3)]^{2+}$ as its ClO_4^-, BF_4^-, or $CF_3SO_3^-$ salts. The kinetics and thermodynamics of Cu(II)/Cu(I) redox also are highly influenced by subtle steric effects as indicated by the large values of $E_{1/2}$ and ΔE_p for $[Cu(L1)]^{2+}$ even though it has a coordination sphere that is superficially similar to $[Cu(L2)]^{2+}$ or $[Cu(L3)]^{2+}$, which have substantially lower values for their electrochemical parameters. Solid-state structures are not necessarily accurate reflections of solution structures, and the square pyramidal complexes reported herein show evidence of structure change upon dissolving that can involve coordination of the anion, solvation, or ligand dissociation depending upon the solvents and anions involved.

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Supplementary Material Available: Text giving details of the structure determinations, bond lengths, bond angles, anisotropic thermal parameters and hydrogen atom parameters (22 pages). Ordering information is given on any current masthead page.