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Structural Demonstration of the Role of Ligand Framework Conformability in Copper(II)/Copper(I) Redox Potentials

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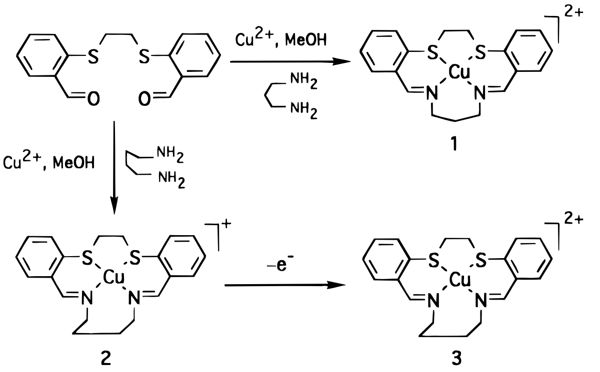
Because of the redox characters of many cuproproteins, the relationship between the geometry around their copper centers and their oxidation states has always been a matter of importance in bioinorganic chemistry.[1,2] For d^{10} Cu(I), the stereochemistry is dictated by the steric and charge effects of the ligands, and so prefers coordination such as tetrahedral or trigonal, while as a d^9 system, Cu(II) adopts stereochemistries providing some crystal field stabilization energy. Sterically demanding ligands tend to stabilize the +1 oxidation state: $[Cu^{II}(6,6'\text{-}Me_2Bipy)_2]^{2+}$ has been reported[3a] to undergo autoreduction in EtOH to the Cu(I) form and the Schiff bases derived from 2-pyridinecarboxaldehyde and 1,6-hexanediamine or bis(2-aminoethyl) disulfide also form air-stable Cu(I) complexes from copper(II) perchlorate.[3b] In a general sense, for macrocyclic Cu(II) complexes, increasing flexibility in the imine linkage favors their electrochemical reduction, while opening the macrocycle might be thought of as corresponding to extrapolation to infinite ring size.[4] Kinetic and thermodynamic studies[5] with N_2S_2 macrocycles also demonstrate the enhanced stability of Cu(I) with more flexible ligands. Although this important aspect of Cu redox chemistry is rather widely accepted, no closely related pair of Cu complexes is available to date, wherein it is demonstrated structurally. We report here Cu(II) and Cu(I) complexes of macrocyclic N_2S_2 ligands which show the appropriate selection of oxidation state with change in ligand flexibility.

The reaction[6] (Scheme 1) of 1,4-bis(2-formylphenyl)-1,4-dithiabutane with equimolar 1,5-diazapentane (1,3-diaminopropane) and $Cu(ClO_4)_2 \cdot 6H_2O$ in refluxing CH_3OH gives dark green **1**, whose solution and solid-state optical spectra are identical. When 1,6-diazahexane (1,4-diaminobutane) is used instead of 1,5-diazapentane, the bright yellow perchlorate or triflate salt **2** is isolated.

Scheme 1



The structural analyses of **1** and **2** (Figures 1 and 2)[8] reveal the geometry around the Cu centers. In **1**, the Cu(II) adopts a square-planar geometry with very little distortion (0.004 Å) of the Cu from the mean plane defined by the S_2N_2 donor set and the least interplanar angle involving Cu and the donor atoms being CuS(1)S(2) and CuN(1)N(2), at 6°. The overall shape of the cation **1** resembles a butterfly, with benzo-wings (interplanar angle 92°). In **2**, the Cu(I) adopts a somewhat

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(6) **1**$(ClO_4)_2$: To 1,4-bis(2-formylphenyl)-1,4-dithiabutane[7] (0.302 g, 1 mmol) suspended in 25 mL of CH_3OH was added a mixture of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.371 g, 1 mmol) and 1,3-diaminopropane (0.074 g, 1 mmol) in 25 mL of CH_3OH. Refluxing the green solution (5 h) produced dark green crystals, which were filtered off, washed with CH_3OH, and recrystallized from CH_3CN/CH_3OH to give diffraction-quality crystals. Yield: 0.48 g (80%). Anal. Calcd for $C_{19}H_{20}N_2Cl_2O_8S_2Cu$: C, 37.9; H, 3.32; N, 4.65. Found: C, 38.2; H, 3.21; N, 4.72. UV−vis (powder): λ_{max}, 407 nm, 590 nm. UV−vis (MeCN): λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) = 275(sh), 400 (3735), 583 (1110). MS(FAB): $m/z = 403$ $[M - 2ClO_4]^{2+}$. **2**$(CF_3SO_3) \cdot CH_3OH$: A mixture of $Cu(CF_3SO_3)_2$ (0.362 g, 1 mmol) and 1,4-diaminobutane (0.088 g, 1 mmol) in 25 mL of CH_3OH was added to a suspension of 1,4-bis(2-formylphenyl)-1,4-dithiabutane (0.302 g, 1 mmol) in 25 mL of CH_3OH. After about 20 min the green reaction mixture became yellow. This conversion of Cu^{2+} to Cu^+ is more rapid in acetonitrile. Following 3 h of reflux, the solution's volume was reduced to about 10 mL (rotavapor); it was allowed to stand overnight and the resulting yellow crystals harvested (0.43 g, 72%). Single crystals were grown by diffusing ether into a CH_3OH solution. Anal. Calcd for $C_{22}H_{26}N_2F_3O_4S_3Cu$: C, 44.1; H, 4.34; N, 4.68. Found: C, 43.9; H, 4.28; N, 4.55. UV−vis (CH_3CN): λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) = 283 (sh), 355 (2770). MS(FAB): $m/z = 417$ $[M - CF_3SO_3]^+$. **3**: Bulk electrolysis of **2**$(CF_3SO_3) \cdot CH_3OH$ in CH_3CN at a Pt-mesh working electrode (NEt_4ClO_4 as supporting electrolyte) at 450 mV *vs* Ag^+ (0.01 M, 0.1 M NEt_4ClO_4, CH_3CN)/Ag gave a deep green solution. Reduction of an aliquot back to **2** with copper powder for measurement of its UV absorbance yielded the molar absorptivities of **3**. UV−vis (CH_3CN): λ_{max}, nm (ϵ, L mol^{-1} cm^{-1}) = 295 (sh), 387 (5450), 615 (1010).

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(8) Crystal data for **1**$(ClO_4)_2$ and, in parentheses, **2**$(CF_3SO_3) \cdot 0.43CH_3OH$: dark green prism (yellow rhombs), $C_{19}H_{20}N_2Cl_2O_8S_2Cu$ ($C_{21.43}H_{23.72}N_2O_{3.43}S_3F_3Cu$), fw = 602.95 (580.91), triclinic (monoclinic), space group *P*1 (No. 2) ($P2_1/n$), $a = 10.566(9)$ Å (7.704(5) Å), $b = 12.671(4)$ Å (22.107(4) Å), $c = 8.766(4)$ Å (14.655(3) Å), $\alpha = 99.89(3)°$, $\beta = 99.41(5)°$ (91.98(3)°), $\gamma = 79.28(5)°$, $V = 1126(1)$ Å^3 (2494(2) Å^3), and $Z = 2$ (4). Data are from a Rigaku AFC6S diffractometer.

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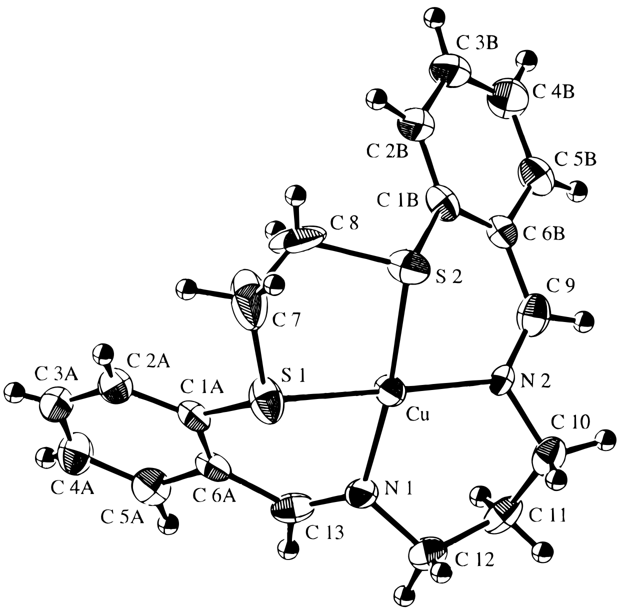

Figure 1. ORTEP drawing for **1**. Selected bond distances (Å) and angles (deg): Cu−S(1) 2.302(2), Cu−S(2) 2.289(2), Cu−N(1) 1.996(6), Cu−N(2) 2.008(4); S(1)−Cu−S(2) 87.48(7), S(1)−Cu−N(1) 88.5(1), N(1)−Cu−N(2) 94.7(2), N(2)−Cu−S(2) 89.7(1), S(1)−Cu−N(2) 175.2(1), S(2)−Cu−N(1) 173.6(1), Cu−O(ClO_4^-) 5.597(5).

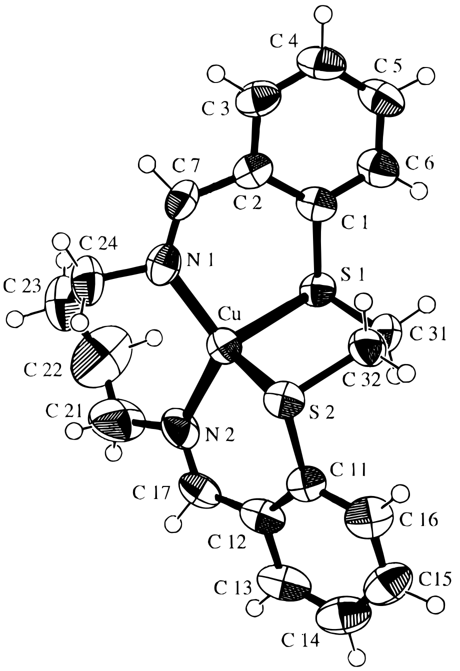

Figure 2. ORTEP drawing for **2**. Selected bond distances (Å) and angles (deg): Cu−S(1) 2.277(2), Cu−S(2) 2.284(2), Cu−N(1) 1.956(5), Cu−N(2) 1.961(5); S(1)−Cu−S(2) 95.64(6), S(1)−Cu−N(1) 98.2(2), N(1)−Cu−N(2) 115.3(2), N(2)−Cu−S(2) 97.6(2), S(1)−Cu−N(2) 127.4(2), S(2)−Cu−N(1) 123.5(2).

Table 1. EPR (77 K) and Electrochemical (298 K) Data[a]

compound[b]	$g_{\parallel}$	$10^4\lvert A_{\parallel}\rvert$	$g_{\perp}$	$(g_{\parallel} - 2)/\lvert A_{\parallel}\rvert$	$E_{1/2}$[f]
$[Cu-(CH_2)_2-](ClO_4)_2$[c,11]	2.278	170	2.04	16	−40[r]
$[Cu-(CH_2)_3-](ClO_4)_2$[d]	2.18	180	2.06	10	+207[q]
$[Cu-(CH_2)_4-](CF_3SO_3)$					+293[q]
$[Cu-(CH_2)_4-]^{2+}$[e]	2.16	190	2.05	8.4	

[a] A in cm^{-1}, $E_{1/2}$ in mV *vs* Ag^+(0.01 M, 0.1 M NEt_4ClO_4, CH_3CN)/Ag in CH_3CN solutions with Pt working and auxiliary electrodes at a scan rate of 100 mV s^{-1}. [b] No. of carbon atoms corresponds to the Schiff base macrocycle formed from the appropriate diamine and 1,4-bis(2-formylphenyl)-1,4-dithiabutane. [c] DMF. [d] CH_3NO_2/MeOH. [e] CH_3NO_2/MeOH/NEt_4ClO_4. [f] Key: q, quasireversible; r, reversible.

flattened tetrahedral geometry, the least dihedral angle (69.5°, involving CuS(1)S(2) and CuN(1)N(2)) acting as an index of the distortion from regular tetrahedral (90°). A noteworthy feature of these two structures is that the Cu−S and Cu−N bonds shorten in passing from Cu(II) to Cu(I), as reported for the Cu(I,II) complexes[9] of 2,5-dithiahexane and 3,6-dithiaoctane. For these latter, the longer Cu(I)−S bond lengths were rationalized in terms of π-back-bonding or the change in coordination number. However, the present study shows that the longer bonds (observed also for the Cu−N linkages) occur despite the constancy of coordination number at 4 for both oxidation states. Indeed, we attribute the increase in bond distances simply to the mechanical consequences of packing the four donor atoms into a plane as opposed to the less mutually repulsive disposition at the apices of the pseudotetrahedron.[10]

The redox potential (Table 1) for the Cu(II)/Cu(I) couple is more positive in **2**, indicating the easier formation of Cu(I) with increasing ligand flexibility. The EPR-based distortion index $(g_{\parallel} - 2)/\lvert A_{\parallel}\rvert$[12] shows (Table 1) that this addition of $-CH_2-$ groups to the imine linkage results in a relaxation of the Cu(II) geometry as well. Indeed, examination of models shows that contrary to the usual situation with acyclic ligands, shorter interimine (or S−S) linkages in these unsaturated N_2S_2 macrocyclic systems actually results in more strain for the square-planar geometry, forcing the metal into a tetrahedral distortion and exaggerating the butterfly motif. The overall outcome is that although ligand flexibility associated with longer N−N or S−S linkages favors a planar geometry around Cu(II), its potential ability to provide a tetrahedral environment to Cu(I) makes the Cu(II)/Cu(I) couple more positive. These results also reflect the potential for enhanced recognition of Cu(I) over Cu(II) by appropriate adjustment of the macrocycle framework.

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Supporting Information Available: Tables of crystal data and refinement details, atomic coordinates and thermal parameters, anisotropic thermal parameters and complete bond distances and angles for **1**$(ClO_4)_2$ and **2**$(CF_3SO_3)\cdot0.43CH_3OH$ (20 pages). Ordering information is given on any current masthead page.

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