

> Fe > Co. As is seen in Figure 5, the metal atom displacements do follow this order. Moreover, the essentially constant Ct...N(NO) (1.93-1.98 Å) and particularly the N...N(NO) nonbonded distances (2.76-2.79 Å) provide confirmation that the nitrosyl nitrogen atom position (and by implication the metal atom position as well) is governed by minimizing the axial nonbonded interactions. We conclude that the minimum N...N nonbonded separation for an axial ligand in five-coordinate metalloporphyrins is ~2.80 Å; thus, structural adjustments must occur to prevent N...N separations significantly less than 2.80 Å.

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Registry No. I-C₆H₆, 68344-27-4; II-CHCl₃, 64399-01-5.

Supplementary Material Available: Listings of the structure factor amplitudes (×10) for both complexes (46 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structures of (1,8-Bis(2-pyridyl)-3,6-dithiaoctane)copper(I) Hexafluorophosphate and Perchlorato(1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) Perchlorate: Stereodynamics of the Copper(II)-Copper(I) Couple

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The crystal and molecular structures of the title compounds have been determined by single-crystal X-ray diffraction using counter data to *R* values of 0.061 for the copper(I) complex (1) and 0.068 for the copper(II) complex (2). The unit cell constants for **1** are *a* = 8.219 (1) Å, *b* = 22.543 (3) Å, and *c* = 11.044 (1) Å; the space group is *Pbcn*, and *Z* = 4. For **2**, *a* = 8.902 (1) Å, *b* = 21.343 (2) Å, *c* = 11.879 (1) Å, β = 108.03 (1)°, the space group is *P2₁/c*, and *Z* = 4. Coordination about **1** is tetrahedral and about **2** is square pyramidal.

We have chosen to approach a description of the copper site of blue proteins via the characterization of reversible copper(II)-copper(I) redox systems. The accumulated evidence suggests that the stereochemistry of the oxidized and reduced species,^{1,2} the presence of sulfur,^{3,4} or the presence of heterocyclic nitrogen donor atoms govern the reversibility and redox potential of the couple. Accordingly, we have reexamined the copper(II) and copper(I) complexes with 1,8-bis(pyridyl)-3,6-dithiaoctane (pdto), first described by Goodwin and Lions about 20 years ago.⁵

Experimental Section

Syntheses. 1,8-Bis(2-pyridyl)-3,6-dithiaoctane, (1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) perchlorate, and (1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(I) hexafluorophosphate were prepared by the methods of Goodwin and Lions.⁵

Electrochemical Methods. Electrochemical measurements were performed on a PAR Model 174A polarographic analyzer equipped with a PAR Model 175 function generator. Hanging mercury drop,

platinum, carbon paste, or gold thin-cell test electrodes were used, as appropriate. A Chemtrix double-junction Ag/AgCl reference electrode was used in all cases, as was 0.1 N KNO₃ supporting electrolyte. Coulometric measurements were made with an Alpha Research Model 701 precision digital current intergrading coulometer.

X-ray Methods. A crystal of the Cu(I) complex was mounted with the [130] axis coincident with the φ axis of a Picker FACS-I diffractometer. Examination of the reciprocal lattice showed *mmm* symmetry and systematic extinctions characteristic of the space group *Pbcn*. Lattice constants were determined by carefully measuring the ±2θ copper radiation doublet from 16 reflections with 2θ > 60°, peak fitting the profiles, and then determining the cell constants by least-squares analysis. The resultant constants are *a* = 8.219 (1), *b* = 22.543 (3), and *c* = 11.044 (1) Å. The calculated density of 1.665 g cm⁻³ for CuC₁₆H₂₀F₆N₂PS₂ agrees with the experimental density 1.66 g cm⁻³ (floatation in CBr₄ and CCl₄) for *Z* = 4.

Three-dimensional intensity data were collected using Ni-filtered Cu Kα radiation on a modified computer-controlled Picker FACS-I diffractometer. A fixed scan rate (2° min⁻¹), variable scan width (2.4° + 0.72 tan θ) θ-2θ scan with 10-s background measurements at the

extremities of the scan was used to measure 1641 independent reflections to a 2θ maximum of 125° . After every block of 50 reflections, three standard reflections were measured to ensure crystal alignment and electronic stability. Structure amplitudes (F_o) and their estimated errors (σ) were calculated from the expressions $F_o = (QI_n)^{1/2}$ and $\sigma^2(F_o) = (-Q/4I_n)[I_s + (t_s/t_b)^2 I_b + (0.2I_n)^2]$, where Q contains corrections for Lorentz-polarization, decay, and absorption, I_s and I_b are the scan and background intensities, t_s and t_b are the scan and background times, and I_n is the net integrated intensity. Absorption was corrected for as a function of ϕ (24% maximum deviation in a ϕ curve at $\chi = 90^\circ$, linear $\mu = 46.5 \text{ cm}^{-1}$) and a linear 2% decay as a function of exposure time. A total of 1179 (71%) of the reflections had $|F_o| > \sigma(F_o)$ and were used in all subsequent calculations.

The experimental details for the Cu(II) complex, with ClO_4 counterions, are similar to those for the Cu(I) complex. The space group was determined to be $P2_1/c$ with $a = 8.902(1) \text{ \AA}$, $b = 21.343(2) \text{ \AA}$, $c = 11.879(1) \text{ \AA}$, and $\beta 108.03(1)^\circ$ from 27 reflections with $2\theta > 49^\circ$. The experimental and calculated densities are both 1.76 g cm^{-3} for $Z = 4$ ($\text{CuC}_{16}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_8\text{S}_2$). Of the 3442 independent reflections measured to $2\theta = 125^\circ$, 2809 (81%) were considered observed and were used in the structure determination and refinement. The crystal exhibited a linear 8.6% decay and had a maximum difference in a ϕ scan at $\chi = 90^\circ$ of 37% (linear $\mu = 59.2 \text{ cm}^{-1}$). **Warning:** (1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) perchlorate is a contact explosive. G.R.B. was defensed for several months by the explosion of about 1 g which detonated while being transferred from a sintered glass funnel.

Structure Determination. The structures of both molecules were determined by the usual heavy-atom method. For the Cu(I) complex, Cu, P, and S atom coordinates were determined from a Patterson map and refined isotropically (minimizing $\sum w(\Delta F)^2$; $w = 1/\sigma^2$) by block-diagonal least squares to $R = 0.44$ ($R = \sum |\Delta F| / \sum |F|$). The scattering factors for all nonhydrogen atoms were from Cromer and Waber,⁶ while that for H was from Stewart, Davidson, and Simpson.⁷ All nonhydrogen atoms were located on subsequent electron density maps and refined isotropically for 15 cycles to $R = 0.13$ and $R_w = 0.15$ ($R_w = [\sum w(\Delta F)^2 \sum w F^2]^{1/2}$). Refinement was continued with anisotropic temperature factors to $R = 0.084$ and $R_w = 0.094$. At this point all hydrogen atoms were easily located from a difference electron density map at heights of approximately 0.3 e/\AA^3 . Anisotropic refinement of the nonhydrogen atoms and coordinate only refinement of the hydrogen atoms with β of the hydrogen atoms fixed at 4.0 \AA^2 were continued until the largest shift in any parameter was less than 0.1 its estimated standard deviation. Attempts to vary the isotropic temperature factors of the hydrogen atoms failed. The final R values, excluding the two reflections [131] and [002] which were too large to measure, are $R = 0.061$ and $R_w = 0.060$ for observed data and $R = 0.087$ and $R_w = 0.063$ for all data.

For the Cu(II) complex, both chlorine and copper coordinates were determined from the Patterson map and the remainder of the nonhydrogen atoms from electron density maps. These atoms were refined isotropically to $R = 0.129$ and $R_w = 0.135$. The temperature factors of the oxygen atoms of the noncoordinated perchlorate group are considerably higher than for the other atoms (10–15 compared to 2–6) and probably indicate a certain degree of disorder. Anisotropic refinement was followed by calculation of a difference electron density map to locate hydrogen atoms. Refinement was continued until convergence at which point $R = 0.068$ and $R_w = 0.066$ for observed data and $R = 0.082$ and $R_w = 0.066$ for all data. The largest peak on a final difference electron density map is 1.0 e/\AA^3 in the vicinity of the noncoordinated perchlorate anion.

Description of the Structures

1. (1,8-Bis(2-pyridyl)-3,6-dithiaoctane)copper(I) Hexafluorophosphate, $[\text{Cu}(\text{pdto})]\text{PF}_6$. The final fractional atomic coordinates and their estimated standard deviations are given in Table I. The $[\text{Cu}(\text{pdto})]^+$ cation is illustrated in Figure 1 and the bond distances and angles are given in Table II. Subject to the steric constraints imposed by the ligand, the inner coordination sphere approximates a tetrahedron, with normal Cu–N distances of 2.04 \AA and Cu–S distances of 2.35 \AA , indistinguishable from the 2.32 \AA average reported for (1,4,8,11-tetrathiacyclotetradecane)copper(I) perchlorate.⁸ The combined effect of 2.35 \AA Cu–S distances and the ethylene bridge joining the sulfur atoms is a reduction of the

Table I. Final Fractional Atomic Coordinates and Their Estimated Standard Deviations ($\times 10^4$) for $[\text{Cu}(\text{pdto})]\text{PF}_6$.

atom	x	y	z
Cu	0.0000 (0)	0.3434 (1)	0.2500 (0)
P	0.0000 (0)	0.0681 (1)	0.2500 (0)
F(1)	-0.0409 (7)	0.1180 (2)	0.1547 (4)
F(2)	-0.0464 (6)	0.0184 (2)	0.1563 (4)
F(3)	0.1812 (6)	0.0680 (2)	0.2072 (5)
N(1)	0.2062 (6)	0.2993 (2)	0.1998 (4)
C(2)	0.3284 (8)	0.3278 (3)	0.1408 (6)
C(3)	0.4475 (8)	0.2971 (3)	0.0804 (6)
C(4)	0.4467 (9)	0.2357 (3)	0.0812 (7)
C(5)	0.3276 (9)	0.2063 (3)	0.1437 (7)
C(6)	0.2110 (8)	0.2392 (3)	0.2020 (6)
C(7)	0.3246 (8)	0.3945 (3)	0.1407 (6)
S(9)	0.0094 (2)	0.4154 (1)	0.4031 (1)
C(8)	0.2047 (8)	0.4224 (3)	0.0543 (6)
C(10)	0.0418 (9)	0.4810 (2)	0.3134 (6)
H(3)	0.5394 (65)	0.3270 (22)	0.0512 (51)
H(4)	0.5281 (66)	0.2133 (22)	0.0436 (50)
H(5)	0.3408 (66)	0.1653 (22)	0.1477 (52)
H(6)	0.1332 (68)	0.2187 (22)	0.2573 (54)
H(7)	0.4385 (66)	0.4060 (23)	0.1296 (53)
H(7')	0.3076 (67)	0.4096 (22)	0.2197 (48)
H(8)	0.1977 (65)	0.4029 (22)	-0.0268 (52)
H(8')	0.2273 (66)	0.4604 (23)	0.0349 (49)
H(10)	0.1647 (65)	0.4822 (23)	0.2996 (46)
H'(10)	0.0072 (70)	0.5137 (21)	0.3611 (48)

Table II. Bond Distances and Bond Angles for $[\text{Cu}(\text{pdto})]\text{PF}_6$.

Distances, \AA			
Cu–N(1)	2.042 (5)	C(2)–C(7)	1.505 (9)
Cu–S(9)	2.345 (1)	C(7)–C(8)	1.508 (9)
N(1)–C(2)	1.360 (8)	C(8)–S(9)	1.829 (7)
C(2)–C(3)	1.373 (9)	S(9)–C(10)	1.800 (6)
C(3)–C(4)	1.385 (10)	C(10)–C(10')	1.560 (9)
C(4)–C(5)	1.369 (9)	P–F(1)	1.578 (4)
C(5)–C(6)	1.373 (10)	P–F(2)	1.572 (4)
C(6)–N(1)	1.355 (8)	P–F(3)	1.563 (5)
Angles, Deg			
N(1)–Cu–N(1')	121.6 (2)	C(8)–S(9)–C(10)	102.3 (3)
S(9)–Cu–S(9')	92.4 (1)	C(8)–S(9)–Cu	102.3 (2)
N(1)–Cu–S(9)	99.7 (1)	C(10)–S(9)–Cu	100.2 (2)
N(1)–Cu–S(9')	120.4 (1)	S(9)–C(10)–C(10')	115.4 (4)
C(2)–N(1)–Cu	120.8 (4)	F(1)–P–F(2)	91.0 (2)
C(2)–N(1)–C(6)	117.4 (5)	F(1)–P–F(3)	90.1 (3)
C(6)–N(1)–Cu	120.4 (4)	F(1)–P–F(1')	89.9 (3)
N(1)–C(2)–C(3)	121.4 (6)	F(1)–P–F(2')	178.2 (3)
N(1)–C(2)–C(7)	117.3 (5)	F(1)–P–F(3')	89.0 (2)
C(3)–C(2)–C(7)	121.2 (6)	F(2)–P–F(3)	91.8 (3)
C(2)–C(3)–C(4)	119.9 (6)	F(2)–P–F(1')	178.2 (3)
C(3)–C(4)–C(5)	119.4 (7)	F(2)–P–F(2')	89.1 (2)
C(4)–C(5)–C(6)	118.3 (6)	F(2)–P–F(3')	88.1 (3)
C(5)–C(6)–N(1)	123.5 (6)	F(3)–P–F(1')	90.0 (2)
C(2)–C(7)–C(8)	115.5 (5)	F(3)–P–F(2')	88.1 (3)
C(7)–C(8)–S(9)	115.5 (5)	F(3)–P–F(3')	180.0 (2)

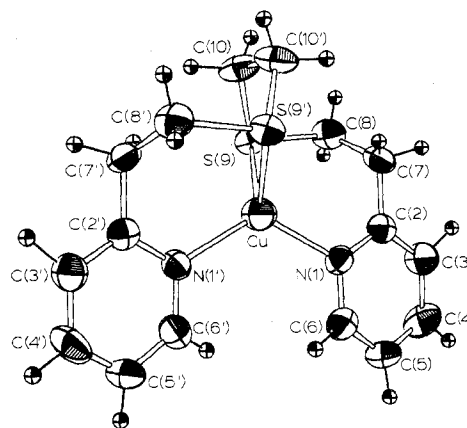
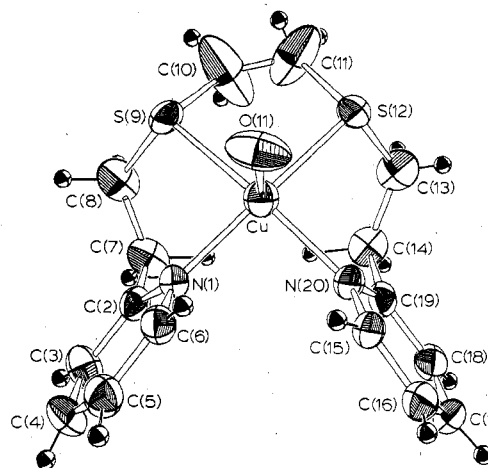


Figure 1. The structure of the (1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(I) cation.

Table III. Final Fractional Atomic Coordinates and Their Estimated Standard Deviations ($\times 10^4$) for $[\text{Cu}(\text{pdto})\text{ClO}_4]\text{ClO}_4$

atom	x	y	z
Cu	0.2600 (1)	0.0822 (0)	0.2024 (1)
N(1)	0.1330 (6)	0.1093 (2)	0.0385 (4)
O(11)	0.4076 (7)	0.0149 (2)	0.1337 (4)
C(2)	-0.0107 (8)	0.1333 (3)	0.0192 (6)
C(3)	-0.0918 (9)	0.1608 (3)	-0.0880 (6)
C(4)	-0.0237 (9)	0.1624 (4)	-0.1775 (6)
C(5)	0.1217 (9)	0.1355 (3)	-0.1590 (6)
C(6)	0.1960 (8)	0.1086 (3)	-0.0515 (6)
C(7)	-0.0832 (8)	0.1287 (4)	0.1171 (7)
C(8)	-0.1173 (9)	0.0614 (4)	0.1437 (7)
S(9)	0.0579 (2)	0.0139 (1)	0.2005 (2)
C(10)	0.0811 (12)	0.0148 (8)	0.3575 (10)
C(11)	0.2185 (14)	0.0196 (5)	0.4344 (7)
S(12)	0.3742 (2)	0.0606 (1)	0.4017 (2)
C(13)	0.3685 (10)	0.1361 (4)	0.4684 (7)
C(14)	0.2914 (9)	0.1883 (3)	0.3840 (7)
C(15)	0.4909 (8)	0.1693 (3)	0.1567 (6)
C(16)	0.5607 (9)	0.2261 (4)	0.1543 (6)
C(17)	0.5401 (9)	0.2735 (3)	0.2249 (7)
C(18)	0.4528 (9)	0.2618 (3)	0.3007 (6)
C(19)	0.3824 (8)	0.2038 (3)	0.2987 (6)
N(20)	0.3971 (6)	0.1588 (2)	0.2243 (5)
Cl(1)	0.4784 (2)	-0.0437 (1)	0.1850 (2)
O(12)	0.6405 (6)	-0.0360 (3)	0.2415 (5)
O(13)	0.4035 (7)	-0.0645 (2)	0.2689 (5)
O(14)	0.4556 (6)	-0.0881 (2)	0.0920 (5)
Cl(2)	0.8761 (3)	0.1653 (1)	0.4760 (2)
O(21)	0.8983 (8)	0.1837 (3)	0.3710 (5)
O(22)	0.7941 (11)	0.2055 (4)	0.5209 (7)
O(23)	0.9995 (10)	0.1394 (6)	0.5491 (6)
O(24)	0.7751 (19)	0.1136 (6)	0.4411 (13)
H(6)	0.2836 (76)	0.0898 (29)	-0.0398 (54)
H(5)	0.1712 (78)	0.1412 (28)	-0.2120 (55)
H(4)	-0.0642 (75)	0.1860 (29)	-0.2290 (54)
H(3)	-0.1911 (77)	0.1765 (28)	-0.1016 (55)
H(15)	0.4906 (78)	0.1384 (29)	0.0998 (56)
H(16)	0.6031 (77)	0.2295 (28)	0.1094 (56)
H(17)	0.5899 (75)	0.3065 (29)	0.2284 (53)
H(18)	0.4211 (75)	0.3085 (29)	0.3583 (54)
H(14)	0.2698 (75)	0.2225 (28)	0.4248 (53)
H'(14)	0.1651 (77)	0.1839 (29)	0.3302 (54)
H(13)	0.3305 (79)	0.1335 (29)	0.5232 (57)
H(13)	0.4696 (79)	0.1373 (29)	0.5002 (56)
H(8)	-0.1740 (78)	0.0594 (29)	0.1841 (56)
H'(8)	-0.1891 (76)	0.0400 (29)	0.0715 (55)
H(7)	-0.1640 (79)	0.1481 (29)	0.0989 (56)
H'(7)	-0.0181 (78)	0.1548 (29)	0.2049 (55)
H(10)	0.0065 (79)	-0.0173 (29)	0.3582 (57)
H'(10)	0.0284 (77)	0.0396 (29)	0.3557 (56)
H(11)	0.2352 (75)	-0.0179 (29)	0.4144 (55)
H'(11)	0.2299 (75)	0.0197 (29)	0.5064 (56)

**Figure 2.** The structure of the perchlorato(1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) cation.**Table IV.** Bond Distances and Bond Angles for $[\text{Cu}(\text{pdto})\text{ClO}_4]\text{ClO}_4$

Distances, Å			
Cu-N(1)	2.011 (5)	S(12)-C(13)	1.804 (8)
Cu-N(20)	2.008 (5)	C(13)-C(14)	1.515 (11)
Cu-S(9)	2.311 (2)	C(14)-C(19)	1.518 (10)
Cu-S(12)	2.316 (2)	C(15)-C(16)	1.367 (10)
Cu-O(11)	2.264 (5)	C(15)-N(20)	1.345 (9)
N(1)-C(2)	1.331 (9)	C(16)-C(17)	1.363 (11)
C(2)-C(3)	1.386 (10)	C(17)-C(18)	1.383 (11)
C(3)-C(4)	1.378 (11)	C(18)-C(19)	1.384 (9)
C(4)-C(5)	1.370 (11)	C(19)-N(20)	1.339 (8)
C(5)-C(6)	1.370 (10)	Cl(1)-O(11)	1.448 (5)
C(6)-N(1)	1.352 (9)	Cl(1)-O(12)	1.400 (6)
C(2)-C(7)	1.498 (10)	Cl(1)-O(13)	1.431 (6)
C(7)-C(8)	1.522 (11)	Cl(1)-O(14)	1.422 (5)
C(8)-S(9)	1.806 (8)	Cl(2)-O(21)	1.379 (7)
S(9)-C(10)	1.813 (12)	Cl(2)-O(22)	1.340 (9)
C(10)-C(11)	1.285 (15)	Cl(2)-O(23)	1.295 (9)
C(11)-S(12)	1.782 (12)	Cl(2)-O(24)	1.402 (13)

Angles, Deg			
N(1)-Cu-N(20)	91.7 (2)	C(11)-S(12)-C(13)	102.3 (4)
S(9)-Cu-S(12)	88.8 (1)	C(11)-S(12)-Cu	101.3 (3)
N(1)-Cu-S(9)	88.2 (2)	C(13)-S(12)-Cu	102.0 (3)
N(20)-Cu-S(12)	88.4 (2)	S(12)-C(13)-C(14)	115.8 (5)
N(1)-Cu-S(12)	170.1 (2)	C(13)-C(14)-C(19)	112.1 (6)
N(20)-Cu-S(9)	162.8 (2)	C(16)-C(15)-N(20)	122.0 (6)
N(1)-Cu-O(11)	92.8 (2)	C(15)-C(16)-C(17)	119.8 (7)
N(20)-Cu-O(11)	99.5 (2)	C(16)-C(17)-C(18)	118.5 (7)
S(9)-Cu-O(11)	97.7 (1)	C(17)-C(18)-C(19)	119.5 (6)
S(12)-Cu-O(11)	97.0 (1)	C(14)-C(19)-C(18)	121.0 (6)
C(2)-N(1)-Cu	120.0 (4)	C(14)-C(19)-N(20)	117.7 (6)
C(2)-N(1)-C(6)	118.7 (6)	C(18)-C(19)-N(20)	121.2 (6)
C(6)-N(1)-Cu	121.1 (4)	C(15)-N(20)-C(19)	118.7 (6)
N(1)-C(2)-C(3)	121.4 (6)	C(15)-N(20)-Cu	121.5 (4)
N(1)-C(2)-C(7)	117.6 (6)	C(19)-N(20)-Cu	119.4 (4)
C(3)-C(2)-C(7)	121.0 (6)	O(11)-Cl(1)-O(12)	110.5 (4)
C(2)-C(3)-C(4)	119.4 (7)	O(11)-Cl(1)-O(13)	109.0 (3)
C(3)-C(4)-C(5)	119.1 (7)	O(11)-Cl(1)-O(14)	108.0 (3)
C(4)-C(5)-C(6)	118.9 (7)	O(12)-Cl(1)-O(13)	109.7 (4)
C(5)-C(6)-N(1)	122.3 (6)	O(12)-Cl(1)-O(14)	109.2 (4)
C(2)-C(7)-C(8)	112.6 (6)	O(13)-Cl(1)-O(14)	110.5 (3)
C(7)-C(8)-S(9)	113.7 (6)	O(21)-Cl(2)-O(22)	115.2 (5)
C(8)-S(9)-C(10)	100.9 (5)	O(21)-Cl(2)-O(23)	113.5 (5)
C(8)-S(9)-Cu	103.3 (3)	O(21)-Cl(2)-O(24)	102.5 (7)
C(10)-S(9)-Cu	98.2 (4)	O(22)-Cl(2)-O(23)	117.3 (5)
S(9)-C(10)-C(11)	120.9 (8)	O(22)-Cl(2)-O(24)	104.1 (7)
C(10)-C(11)-S(12)	121.2 (8)	O(23)-Cl(2)-O(24)	101.3 (8)

normal tetrahedral S(9)-Cu-S(9') angle to 92.4°. "Pinching" two tetrahedral apices together in this fashion results in an opening of the opposite edge, so that the N(1)-Cu-N(1') angle is 121.60°. The constraints of the ethylene bridges joining the pyridine ring with the sulfur atoms reduce the dihedral angle between the S-Cu-S and N-Cu-N planes to 74.5° (from the tetrahedral angle of 90°). All of the bond angles and distances within the ligand system are within the range observed for similar molecules, and there are no significant intermolecular contacts within 3.2 Å. The hexafluorophosphate anion appears as a regular octahedron (P-F distance 1.57 Å) lying along the twofold axis with the phosphorus atom 6.2 Å from the copper(I) ion.

2. Perchlorato(1,8-bis(2-pyridyl)-3,6-dithiaoctane)copper(II) perchlorate, $[\text{Cu}(\text{pdto})\text{ClO}_4]\text{ClO}_4$. The final fractional atomic coordinates and their estimated standard deviations are given in Table III. The structure of the $[\text{Cu}(\text{pdto})\text{ClO}_4]^+$ cation is shown in Figure 2; bond distances and angles are given in Table IV. The structure is essentially square pyramidal, with the nitrogen and sulfur atoms occupying the

basal plane and a perchlorate oxygen bound to the apex. The copper ion is displaced some 0.25 Å from the least-squares plane of the nitrogen and sulfur donors in the direction of the perchlorate ion; none of the other donor atoms deviates from this plane by more than 0.07 Å.

The observed Cu–N distances (2.011 (5) Å) are within 3σ of those found by Wright and Quinn⁹ for the complex diperchlorato(1,8-bis(2-pyridyl)-3,6-diazaoctane)copper(II), [Cu(pdao)(ClO₄)₂] (2.017 (4) Å), and by Lewis and Hodgson¹⁰ for the complex diperchlorato[bis(2-(2-aminoethyl)pyridine)]copper(II) (2.024 (2) Å). The observed copper–sulfur distances (2.311 (2), (2.316 (2) Å) are indistinguishable from those found by Glick et al.,⁴ for the tetrathia ether macrocyclic complex diperchlorato(1,4,8,11-tetrathia-cyclotetradecane)copper(II) (2.308 (1), (2.297 (1) Å). The copper–oxygen distance (2.264 (5) Å) is significantly shorter than typical of copper(II) perchlorate complexes (2.52–2.68 Å). We have observed no anomalous distances or angles within the hydrocarbon moiety.

The overall ligand conformation is somewhat saddle shaped, without any discernible tetrahedral distortion in contrast with the structure of the closely related complex [Cu(pdao)(ClO₄)₂]. The conformation of the ligand in [Cu(pdao)(ClO₄)₂] resembles a shallow helix, with the pyridyl nitrogen atoms displaced 0.79 Å above and below the plane of the copper ion and secondary aliphatic nitrogen donors. In this conformation, the hydrogen atoms bound to the pyridine C(6) and C(15) atoms are separated by 2.96 Å along a vector roughly parallel the Cu–ClO₄ bonds, indicating that the helical conformation is a consequence of steric hindrance between these protons. The angle between the plane of the copper and pyridyl nitrogens and that of the copper and secondary nitrogens is 31.9°, about midway between the trans-octahedral angle (0°) and that found for [Cu(pdto)]⁺ (74.5°) (vide infra). We had expected to find a similar structure for [Cu(pdto)ClO₄]⁺ as part of our study of the relationship between tetrahedral distortions of copper(II) complexes and redox potential. In fact, we find that the H(C6)–H(C15) distance is only 2.3 Å, quite comparable with the distances between adjacent hydrogen atoms bound to the pyridine nucleus.

The angles around the pyridine nitrogen atoms are all 120° within experimental uncertainty, indicating very little distortion from the expected sp² character of these atoms. This suggests that the copper sits above the mean plane of the nitrogen and sulfur donors at the point which the ligand orbitals intersect; the short Cu–O distance reflects, primarily, Coulombic effects on the single anionic ligand (as compared with distances in diperchlorato complexes).

Space-filling molecular models suggest that it would be difficult to add a sixth ligand, since the other observed metal–donor distances are normal and the metal ion lies above the plane of the neutral donors (away from the “vacant” coordination site).

Electrochemical Studies. The formal redox potential E_0' (from cyclic voltammetry in 0.1 M aqueous KNO₃ on a carbon paste electrode at 20 mV/s) is +0.577 V. The separation between the anodic and cathodic peaks of the cyclic voltammogram is 0.117 V, and the peaks are broad, suggesting that electron transfer is accompanied by another, slower process, quite possibly a stereochemical change in solution linking the structures observed in the solid state. In spite of the non-Nernstian behavior manifested in the large separation between the anodic and cathodic peaks, coulometric measurements have shown that the complex can be quantitatively reoxidized following reduction at the carbon paste electrode.

The +577 mV reduction potential of [Cu(pdto)ClO₄]⁺ demonstrates that tetrahedral distortion of the coordination sphere is not required in order to achieve a fully reversible copper(II)–copper(I) couple with a positive potential. Similar conclusions have been drawn by Rorabacher from his studies of planar tetrathia macrocyclic complexes with copper.⁴

The electronic spectrum of the cation [Cu(pdto)]²⁺ (λ_{\max} 605 nm, ϵ 510 M⁻¹ cm⁻¹) and EPR parameters ($g_0 = 2.091$, $A_0 = 7.00 \times 10^{-3}$ cm⁻¹; $g_{\parallel} = 2.176$, $A_{\parallel} = 6.66 \times 10^{-3}$ cm⁻¹; $g_{\perp} = 2.058$, $A_{\perp} = 2.17 \times 10^{-3}$ cm⁻¹) are more similar to those of other low molecular weight model complexes than to those of “blue” proteins (for parsley plastocyanin, λ_{\max} 597 nm, $\epsilon \sim 5000$ M⁻¹ cm⁻¹; $g_0 = 2.06$; $g_{\parallel} = 2.23$; $A_{\parallel} = 6.56 \times 10^{-3}$ cm⁻¹). The copper(I) complex is both colorless and diamagnetic.

Conclusions

We have described the structures of monomeric copper(I) and copper(II) complexes with a common ligand. This work is the first reported structural study of copper complexes in two oxidation states with precisely the same ligand.¹² The title compounds are of particular interest in light of very recent reports of the solution of the structures of poplar plastocyanin by Freeman et al.¹³ and of an azurin from *Pseudomonas aeruginosa* by Seiker et al.¹⁴ The protein structures (at 2.7 and 3 Å, respectively) show clearly that the copper ion is bound to two nitrogen (His) and two sulfur (Cys, Met) donor atoms in each case. At the present level of refinement, the exact coordination geometry is uncertain, and in the case of azurin (but not plastocyanin) there remains a possibility that a fifth residue may be coordinated with the copper ion. Water molecules could be in the coordination sphere of the copper ion in either protein.

In view of the close similarity of the donor atoms of these complexes (two heterocyclic nitrogen atoms from pyridine, two thioether sulfur atoms) to those of plastocyanin and azurin (two heterocyclic nitrogen atoms from histidine, one sulfur from cysteine, one sulfur from methionine), we regard the title compounds as superior models for the copper site of blue proteins. We propose that a steric change accompanying electron transfer in blue proteins, analogous to the structural differences we report here, contributes to the unique electron transport properties of type 1 copper proteins.

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Supplementary Material Available: Listings of the anisotropic temperature factors and structure factor amplitudes for both molecules (27 pages). Ordering information is given on any current masthead page.

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