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A Stable Bis(thiolate) of Copper(II) with Long Axial Copper–Sulfur Linkages: Crystal and Molecular Structure of *trans*-[Cu(cyclam)$(SC_6F_5)_2$]

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With pentafluorothiophenolate in alcohol solvents, the (1,4,8,11-tetraazacyclotetradecane)copper(II) cation, $Cu(cyclam)^{2+}$, is not reduced but yields the red complex $Cu(cyclam)(SC_6F_5)_2$, which crystallizes in the space group $P\bar{1}$. The cell constants are $Z = 1$, $a = 7.140$ Å, $b = 8.320$ Å, $c = 12.033$ Å, $\alpha = 75.02°$, $\beta = 88.97°$, $\gamma = 71.07°$, $V = 651$ Å^3, and $\rho_{obsd} = 1.65$ g cm^{-3}, with $R_w = 5.5\%$. The sexicoordinate complex is tetragonally elongated, with equatorial Cu–N bonds of 2.005, 2.011, 2.005, and 2.011 Å in a square arrangement. The axially disposed thiolate anions are weakly bonded, with Cu–S distances of 2.94 Å, comparable with the axial Cu–S bond in plastocyanin. The optical and ESR spectra of the complex reveal no characteristic effects of the axial thiolates on the electronic properties of the Cu(II) ion.

Introduction

Simple thiolate (mercaptide) complexes of copper(II) are usually thermodynamically unstable with respect to their Cu(I) and disulfide redox products. However, the presence of Cu(II)–thiolate linkages in plastocyanin[2] and azurin[3] has provided further impetus for the development of strategems to synthesize such classes of compounds.

The Cu(II)–thiolate state has been stabilized by the introduction of multiple-bond character at the donor sulfur[4] and by the delocalization of higher oxidation state charge in mixed-valence Cu–S clusters.[5] Kinetic barriers against the redox process have been erected by performing experiments under cryogenic conditions[6,7] or by imposing steric hindrances.[8,9]

Nonetheless, there are few examples of simple thiolate complexes of copper(II), among which only two cases of a mononuclear complex have been structurally characterized, both of them 1:1 in Cu(II):thiolate.[10,11] We report here a simple synthesis and the X-ray crystal structure of a stable 1:2 Cu(II):thiolate complex, derived from $[Cu(cyclam)]^{2+}$, the chelate of the macrocycle **1** (Figure 1).

The synthesis logic entails a number of elementary components. The thermodynamics of the redox reaction between Cu(II) and RS^- should be disfavored if the potential of the Cu(II)/Cu(I) couple is depressed and the potential of the $RSSR/RS^-$ couple is raised. Electron-withdrawing substituents presumably effect the latter; para nitration raises the reductive $E_{1/2}$ of diphenyl disulfide by 0.5 V,[12] and ring perfluorination has been shown to lower the HOMO energy of benzenethiol by ca. 100 kJ.[13] For copper, cyclam greatly stabilizes Cu(II) relative to Cu(I),[14] so that in some solvents, Cu(I) species are not isolable.[15]

Kinetically, it is expected that the square-planar stereochemistry that cyclam imposes at Cu(II) should inhibit the formation of any binuclear intermediate of the type $[Cu_2(SR)_2]$, which provides the redox-complementary pathway to the disulfide product.[16]

Amundsen et al.[8] reported that the presumably more reducing isopropyl mercaptide, in large excess, produced bands in the absorption spectrum of $Cu(cyclam)^{2+}$ attributable to $S(\sigma) \rightarrow Cu(II)$ charge transfer, as well as a pentaammine type of effect, in the relatively redox unstable $[Cu(cyclam)(S\text{-}i\text{-}Pr)]^+$ product.

Experimental Section

Amines (Strem), metal perchlorates (G. F. Smith), and pentafluorothiophenol (Aldrich) were used as received.

Bis(pentafluorothiophenolato)(1,4,8,11-tetraazacyclotetradecane)copper(II), $Cu(cyclam)(SC_6F_5)_2$, was prepared by adding a warm solution of pentafluorothiophenol (0.90 g, 4.5 mmol) and sodium hydroxide (0.8 mL of 5 M aqueous solution) in 2-methoxyethanol (10 mL) to a hot, filtered solution of cyclam (0.40 g, 2 mmol) and hydrated copper(II) perchlorate (0.37 g, 2 mmol) in 85% aqueous 2-methoxyethanol (25 mL). The rose-pink prisms that separated in >95% yield were filtered off, washed with methanol, and dried in vacuo over P_4O_{10}. Anal. Calcd for $C_{22}H_{24}CuF_{10}N_4S_2$: C, 39.9; H, 3.65; N, 8.46. Found: C, 40.0; H, 3.57; N, 8.43.

The cream, crystalline **zinc(II) compound** $Zn(Cyclam)(C_6F_5S)_2 \cdot 2C_6F_5SH$ was prepared analogously, but with use of neat methanol as solvent throughout. Anal. Calcd for $C_{34}H_{26}F_{20}N_4S_4Zn$: C, 38.4; H, 2.46; N, 5.27. Found: C, 38.2; H, 2.26; N, 5.41. The infrared spectrum displayed a band of weak to medium intensity at 2430 cm^{-1}, attributable to S–H stretching; there was no absorption associable with S–S stretching of a disulfide.

Optical and infrared spectra were obtained on Perkin-Elmer 320 and 457 instruments, respectively, and electron spin resonance spectra with a Varian E-12 X-band spectrometer. Elemental microanalyses were performed by the Canadian Microanalytical Service Ltd. (Vancouver). ESR spectra were simulated with the program SIM-14/14a (QCPE), adapted for an IBM 370; Gaussian line widths used are symbolized by ω in the text.

Crystal Data and Data Collection: $CuS_2F_{10}N_4C_{22}H_{24}$, mol wt 662, space group $P\bar{1}$, $Z = 1$, $a = 7.140\ (4)$ Å, $b = 8.320\ (5)$ Å, $c = 12.033\ (9)$ Å, $\alpha = 75.02\ (3)°$, $\beta = 88.97\ (4)°$, $\gamma = 71.07\ (5)°$, $V = 651$ Å^3, $\rho_{calcd} = 1.69$ g cm^{-3}, $\rho_{obsd} = 1.65$ g cm^{-3}, $\mu(Mo\ K\alpha) = 11.3$ cm^{-1}; crystal

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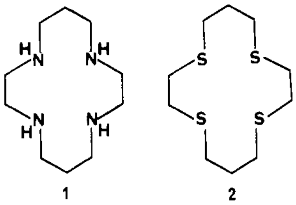

Figure 1. Cyclam (**1**) and its sulfur analogue (**2**).

Table I. Positional Parameters and Their Estimated Standard Deviations for Cu(cyclam)$(SC_6F_5)_2$

atom	*x*	*y*	*z*
Cu	0.0000 (0)	0.0000 (0)	0.0000 (0)
S	0.3095 (2)	0.1167 (3)	−0.1262 (1)
F(2)	0.2504 (7)	0.4812 (6)	−0.2779 (4)
F(3)	0.2275 (9)	0.5816 (10)	−0.5063 (5)
F(4)	0.2339 (9)	0.3562 (11)	−0.6340 (4)
F(5)	0.2736 (8)	0.0211 (8)	−0.5258 (4)
F(6)	0.3157 (7)	−0.0922 (6)	−0.2980 (4)
N(1)	0.2106 (6)	−0.1021 (6)	−0.1307 (4)
N(5)	0.0932 (6)	−0.2093 (6)	−0.0658 (4)
C(2)	0.2581 (9)	−0.2898 (10)	0.1839 (6)
C(3)	0.3259 (10)	−0.4032 (9)	0.1010 (7)
C(4)	0.1664 (9)	−0.3829 (8)	0.0128 (6)
C(6)	−0.0683 (9)	−0.1891 (8)	−0.1509 (5)
C(7)	−0.1562 (8)	−0.0007 (8)	−0.2143 (5)
C(R1)	0.2843 (8)	0.1898 (10)	−0.2758 (5)
C(R2)	0.2590 (9)	0.3601 (11)	−0.3344 (6)
C(R3)	0.2488 (12)	0.4215 (13)	−0.4548 (8)
C(R4)	0.2485 (12)	0.3009 (14)	−0.5171 (7)
C(R5)	0.2722 (11)	0.1389 (11)	−0.4656 (6)
C(R6)	0.2888 (9)	0.0781 (10)	−0.3448 (6)
H1	0.311 (7)	0.896 (7)	0.103 (4)
H21	0.363 (8)	−0.314 (8)	0.247 (5)
H22	0.143 (8)	−0.306 (7)	0.214 (5)
H31	0.401 (7)	−0.528 (7)	0.132 (4)
H32	0.418 (9)	−0.363 (9)	0.068 (5)
H41	0.214 (9)	−0.464 (8)	−0.031 (5)
H42	0.057 (9)	−0.404 (9)	0.053 (5)
H5	0.201 (8)	0.829 (7)	0.886 (5)
H61	−0.020 (11)	−0.249 (10)	−0.202 (6)
H62	−0.158 (10)	−0.255 (9)	−0.097 (6)
H71	0.250 (8)	−0.019 (7)	0.267 (5)
H72	0.944 (8)	−0.003 (7)	0.741 (5)

Table II. Bond Lengths and Selected Intermolecular Contacts (Å)

Cu-S	2.940 (1)	N(5)-C(6)	1.495 (5)
Cu-N(1)	2.005 (3)	C(6)-C(7)	1.481 (7)
Cu-N(5)	2.011 (3)	⟨C(R)-C(R)⟩[a]	1.374 (8)
S-C(R1)	1.737 (5)	⟨F-C(R)⟩[b]	1.333 (7)
N(1)-C(2)	1.452 (7)	⟨C-H⟩[c]	0.94
C(2)-C(3)	1.515 (7)	F(4)-C(2)	3.238 (8)[d]
C(3)-C(4)	1.509 (6)	F(5)-F(5)	3.191 (8)[e]
C(4)-N(5)	1.441 (7)	F(5)-C(R5)	3.091 (6)[e]

[a] Average phenyl C-C distance. [b] Average F-C distance. [c] Average C-H distance. [d] Symmetry transformation x, $y + 1$, $z - 1$. [e] Symmetry transformation $1 - x$, $-y$, $-1 - z$.

Table III. Bond Angles and Their Standard Deviations (deg)

S-Cu-S′	180.0	Cu-N(5)-C(6)	106.8 (3)
S-Cu-N(1)	83.0 (1)	C(4)-N(5)-C(6)	113.2 (4)
S-Cu-N(1′)	97.1 (1)	N(5)-C(6)-C(7)	109.2 (4)
S-Cu-N(5)	86.3 (1)	S-C(R1)-C(R2)	122.8 (4)
S-Cu-N(5′)	93.7 (1)	S-C(R1)-C(R6)	122.2 (5)
N(1)-Cu-N(1′)	180.0	F(2)-C(R2)-C(R1)	120.9 (5)
N(1)-Cu-N(5)	94.8 (1)	F(2)-C(R2)-C(R3)	114.8 (7)
N(1)-Cu-N(5′)	85.2 (1)	F(3)-C(R3)-C(R2)	122.4 (7)
N(5)-Cu-N(5′)	180.0	F(3)-C(R3)-C(R4)	116.5 (7)
Cu-S-C(R1)	120.0 (2)	F(4)-C(R4)-C(R3)	118.4 (8)
Cu-N(1)-C(2)	115.2 (3)	F(4)-C(R4)-C(R5)	120.3 (7)
N(1)-C(2)-C(3)	114.0 (4)	F(5)-C(R5)-C(R4)	121.3 (6)
C(2)-C(3)-C(4)	114.6 (4)	F(5)-C(R5)-C(R6)	117.2 (7)
C(3)-C(4)-N(5)	113.6 (4)	F(6)-C(R6)-C(R1)	120.8 (5)
C(4)-N(5)-C(6)	113.2 (4)	F(6)-C(R6)-C(R5)	117.8 (5)
Cu-N(5)-C(4)	118.5 (3)	⟨C-C-C⟩	120.0 (6)

dimensions (distances in mm of faces from centroid) (100) 0.175, ($\bar{1}00$) 0.175, (010) 0.004, ($0\bar{1}0$) 0.004, (001) 0.06, ($00\bar{1}$) 0.06; maximum, minimum transmission coefficients 0.99, 0.93.

Cell dimensions and space group data were obtained by standard methods on an Enraf-Nonius four-circle CAD-4 diffractometer. The θ–2θ scan technique was used, as previously described,[17] to record the intensities for all nonequivalent reflections for which $1.5° < 2\theta < 57°$. Scan widths were calculated as $(A + B \tan \theta)°$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of peak due to $K\alpha_1$–$K\alpha_2$ splitting. The values of A and B were 0.50 and 0.35, respectively.

The intensities of four standard reflections, monitored at 100-s reflection intervals, showed no greater fluctuations than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects and absorption. Of the 2344 independent intensities, there were 1609 with $F_o^2 > 3\sigma(F_o^2)$, where $\sigma(F_o^2)$ was estimated from counting statistics.[18] These data were used in the final refinement of the structural parameters.

Structure Determination. The unit cell size and a three-dimensional Patterson function indicated that the metal atom must reside at the cell origin of a $P1$ or $P\bar{1}$ unit cell. $P\bar{1}$ was chosen and verified by subsequent refinement. The intensity data were phased sufficiently well by the positional coordinates of the copper atom to permit location of the other non-hydrogen atoms from Fourier syntheses. Full-matrix least-squares refinement was carried out as previously described.[17] Anisotropic temperature factors were introduced for all non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for three cycles of least-squares and then held fixed. The model converged with $R = 5.1\%$, $R_w = 5.5\%$. A final Fourier difference function was featureless. The principal programs used were as previously described.[17]

Results and Discussion

On the basis of the previously reported 1:1 Cu(II):thiolate systems, one might have expected that Cu(cyclam)$(SC_6F_5)(ClO_4)$ would form readily, but the bis(thiolate) was still the sole product of syntheses in which a 1:1 ratio of Cu(II):thiolate was used.

We have also observed, that neither (*N,N′,N″,N‴*-tetramethylcyclam)copper(II) nor (triethylenetetramine)copper(II) forms a pentafluorothiophenolate of stability as prolonged as that of Cu(cyclam)$^{2+}$. Both are reduced to copper(I) species by the thiolate, as evidenced by the latter's bleaching of the metal d–d bands. A thiophenolate with less electronegative substitution (*p*-chlorothiophenolate) also reduces Cu(cyclam)$^{2+}$ in methanol, although a purple transient is formed.

The structure of the cyclam–pentafluorothiophenolate complex (Figure 2) confirms the analytical composition and shows that the two thiolate sulfur atoms are axially trans, at the central copper(II).

The bond lengths (Table II) in the coordination sphere reflect the classical axially elongated stereochemistry of sexicoordinate Cu(II), with the cyclam nitrogens all being strongly bonded at 2.01 Å in an essentially square arrangement (Figure 2), quite comparable with the situation in Cu(cyclam)$(ClO_4)_2$.[19]

The axial Cu-S distances (2.94 Å) are long in comparison with those in the two pentacoordinate 1:1 thiophenolate complexes (2.42, 2.36 Å).[10,11] This result is not an intrinsic property of pentafluorothiophenolate, as a cobalt(II) complex with this anion has a more "normal" bond length of 2.26 Å.[20]

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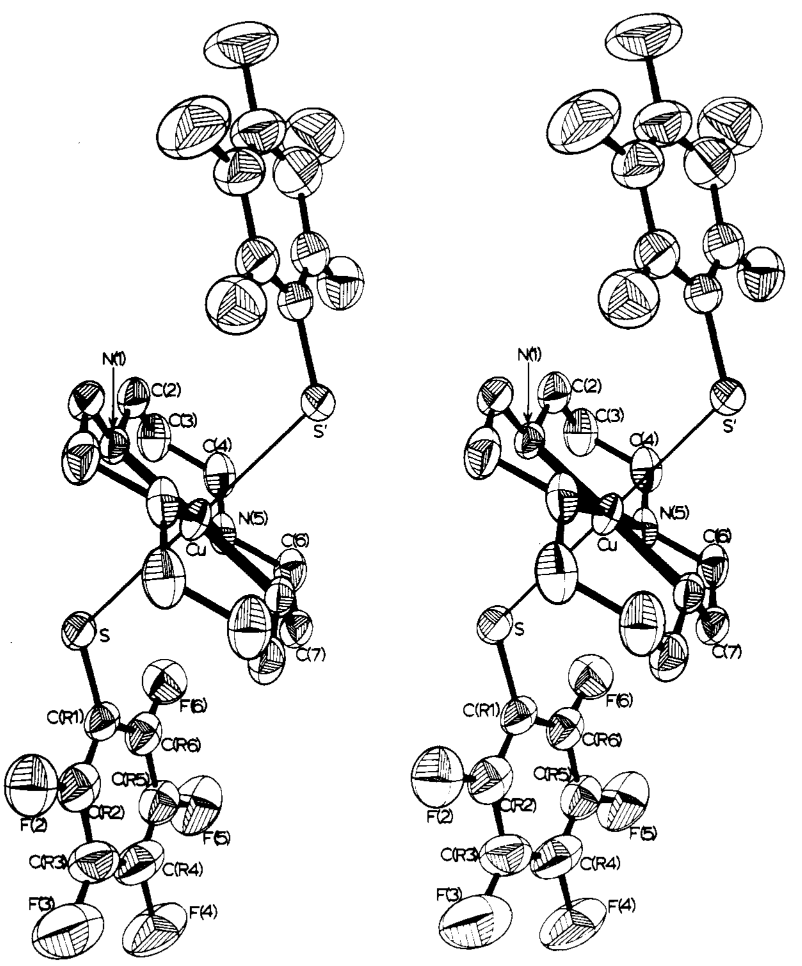

Figure 2. Stereoview of Cu(cyclam)(SC_6F_5)$_2$, showing the atomic numbering scheme. Hydrogen atoms are omitted for clarity of presentation.

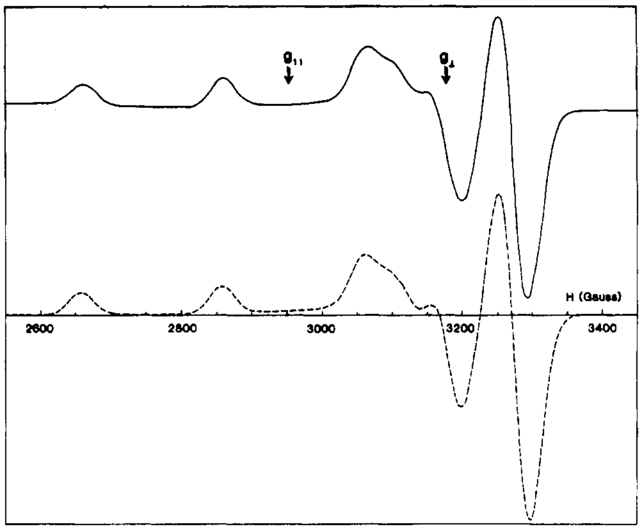

Figure 3. 77 K X-band ESR spectrum of the complex, in DMF, with excess pentafluorothiophenolate (solid trace), and the spectrum simulated (broken trace) by using the parameters in the text and $\omega_{\parallel}$ = 36 G, $\omega_{\perp}$ = 47 G.

In-plane thioether–Cu(II) linkages are also considerably shorter: 2.30 Å in the perchlorate salt of the tetragonal Cu(II) chelate of the macrocycle **2**.[21] Only disulfide sulfur has been observed to interact more weakly with Cu(II), the axial Cu–S distances observed (3.1–3.2 Å)[22,23] probably constituting little more than nonbonded interactions. In fact, the axial Cu–O bonds in Cu(cyclam)(ClO_4)$_2$ are 0.37 Å shorter.[19]

Table IV. Optical Spectra of M(cyclam)X_2

M	X (medium)	λ, nm (ε, M^{-1} cm^{-1})
Cu	(a) ClO_4^- (DMF)	520 (85)
Cu	(b) thiolate (DMF)	520 (77)
Cu	(c) = (b) − (a)	800 (5) 540 (18) 335 (5800)
Cu	thiolate (Nujol mull)	520 400 (sh)
Cu	ClO_4^- (Nujol mull)	510
Zn	thiolate (DMF)	340 (1700) 276 (1900)

It thus appears, that the S–Cu interactions in the title compound are likely to be essentially ionic in nature.

The Cu–S linkages are bent slightly off the perpendicular to the CuN_4 plane by 4–7° (Table III). The angle at sulfur (120.0°) is larger in comparison with the other two arenethiolates (101°,[10] 108°[11]), while the phenyl ring is canted at about 67° to the CuSC plane. The larger CuSC angle may indicate the reduced importance of well-directed hybridization at the donor sulfur in Cu(cyclam)(SC_6F_5)$_2$.

The relatively noncovalent nature of the metal–sulfur linkages is also suggested by the electron spin resonance of the complex both in DMF solution with excess thiolate present (Figure 3: $g_{\parallel}$ = 2.200, $g_{\perp}$ = 2.050, $10^4A_{\parallel}$ = 205 cm^{-1}, $10^4A_{\perp}$ = 30 cm^{-1}, 77 K) and as a 5% dopant in the zinc compound ($g_{\parallel}$ = 2.166, $g_{\perp}$ = 2.039, $10^4A_{\parallel}$ = 205 cm^{-1}, $10^4A_{\perp}$ = 29 cm^{-1},

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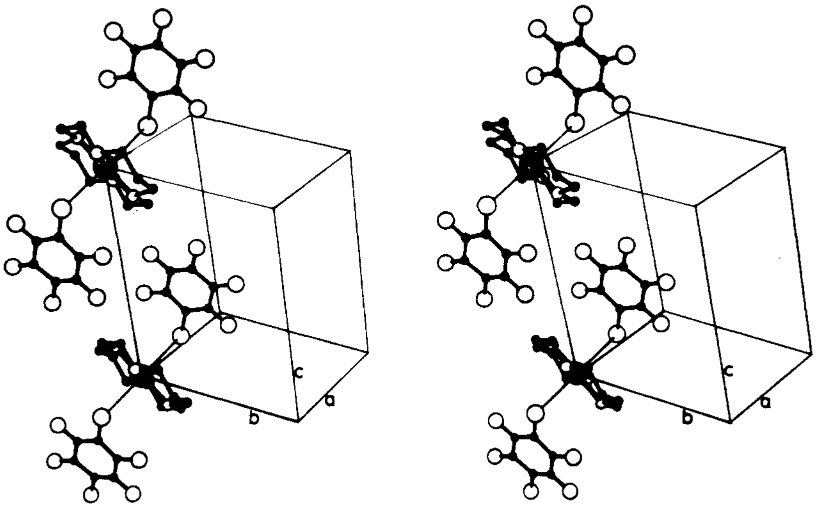

Figure 4. Stereoview of the Cu(cyclam)(SC_6F_5)$_2$ unit cell (hydrogens omitted).

300 K). The unit cell dimensions (Figure 4) are such that the pure copper complex ($g_\parallel = 2.217$, $g_\perp = 2.05$) is not magnetically dilute, within the ESR energy regime, so that the usual situation (hfs not observed) pertains.

The close similarity of the former spectra with the ESR of Cu(cyclam)(ClO_4)$_2$ in DMF ($g_\parallel = 2.194$, $g_\perp = 2.052$, $10^4A_\parallel = 206$ cm^{-1}, $10^4A_\perp = 29$ cm^{-1}, 77 K) shows that the principal plane (equator) remains associated with a CuN_4 core in the pure complex, in its solution, and in the doped lattice of the Zn(II) compound. The latter is inferred not to have a folded, cis-configured ligand, for example. the $A_\perp$ values in particular[24] indicate similarly weak z-axial interaction in all three situations. This is corroborated by the optical spectra (Table IV) for which only slight differences are seen between the perchlorate and the pentafluorothiophenolate in the visible region in both the solid and solution states; indeed, crystalline Cu(cyclam)(ClO_4)$_2$ and Cu(cyclam)(SC_6F_5)$_2$ are very similar in color.

No *strong* absorptions attributable to S → Cu LMCT are observable for the (thiolato)copper(II) complex, though there *is* a shoulder in the solid-state spectrum at about 400 nm. In this region, difference spectrophotometry between the copper thiolate and the copper perchlorate (in DMF solutions) reveals a band at 335 mn in the thiolate, but this is also present in the UV spectrum of the zinc(II) complex. A broad, weak shoulder near 800 nm (seen in the difference spectrum) is most likely attributable to crystal field transitions in a 1:1 complex formed by ligand dissociation equilibria.[8,24]

Because cyclam imposes a highly tetragonal crystal field at the central atom, the energy of the ground-state $d_{x^2-y^2}$ orbital is considerably raised (as evidenced to an extent by the low $E_{1/2}$) relative to many other copper(II) complexes. Stabilization of the sulfur donor orbitals by perfluorination of the thiolate is likewise expected to contribute to increasing the energy required for sulfur-to-copper charge transfer, thus destabilizing both potential Cu(I)–disulfide ground-state redox reaction products, and also the LMCT excited state. The role of these energetic considerations in the observability of LMCT in the optical spectrum is, however, most likely overshadowed by orbital-overlap considerations. Schugar and co-workers[25] have presented good evidence that the relatively poor overlap of axial sulfur donor orbitals with the equatorially disposed $d_{x^2-y^2}$ Cu(II) acceptor orbital leads to low LMCT band intensity. The title complex appears to offer further vindication of this viewpoint.

These results show that even mercaptide sulfur, if bound at length axially to copper(II), does not contribute characteristically to the spectroscopic properties of the metal. Clearly, a thioether sulfur bound axially to copper(II) at a like distance will also contribute little to the spectroscopy of the copper that is in any way characteristic of the donor atom.

One may note that, in this regard, Cu(cyclam)(SC_6F_5)$_2$ offers itself as an excellent model for the axial Cu–S (methionine) interaction in the type-I copper of *Populus nigra italica* plastocyanin, in which the published Cu–S distance is estimated[26] to be the same (within 2%) as in the small-molecule complex. The corresponding linkage in *Pseudomonas aeruginosa* azurin, though, may be significantly shorter.[27]

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Registry No. Cu(cyclam)(SC_6F_5)$_2$, 84850-89-5; Zn(cyclam)(SC_6F_5)$_2$, 84850-90-8.

Supplementary Material Available: Tables V (bond distances and angles with estimated standard deviations), VI (observed and calculated structure factors), and VII (thermal parameters and their standard deviations) (10 pages). Ordering information is given on any current masthead page.

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