mono(μ-hdyroxo) copper(II) complexes. In this latter case, however, CuOCu is always found larger than 110° and the interaction is always antiferromagnetic.[30]

(ii) In bis(μ-phenolato) copper(II) dimers, the interaction is always strongly antiferromagnetic with S–T energy gaps in the range 400–700 cm^{-1}.[31-32] Although, to our knowledge, no clear dependence of the magnitude of the interaction vs. the value of the bridging angle has been reported so far, a trend similar to that observed with hydroxo-bridged compounds may be expected.

(iii) In the two copper(II) complexes reported so far[6,7,33] with two end-on azido bridges, the triplet state has been found to be the ground state, its stabilization with regard to the singlet state being of the order of 100 cm^{-1}. In addition, a μ-hydroxo, μ-1,1-azido complex has also been described, in which the triplet state is stabilized by more than 200 cm^{-1} with regard to the singlet state.[5] These results clearly indicate that the end-on azido bridge has quite a remarkable ability to favor a ferromagnetic interaction. This property has been attributed to a spin polarization effect.

From the considerations above, one qualitatively understands the nature and the magnitude of the interaction in **1**. The two CuOCu linkages favor the pairing of the electrons. Indeed, on the hydroxo side, the CuOCu angle is 99.3°. Since the values of the two bridging angles are of the same order of magnitude, there is no antisynergic effect. Likely, the stabilization of the singlet state would be more pronounced if the bridging angle on the phenolato side was larger.

More interesting is the situation in **2**. The antiferromagnetic contribution due to the phenolato bridge may be expected to be larger than in **1** due to the fact that the CuOCu angle is significantly larger (98.7° instead of 97.4°). On the other hand, the end-on azido bridge exerts a ferromagnetic contribution, so that altogether the singlet state is much less stabilized than in **1** with $J = -86.5$ cm^{-1}.

In **3**, finally, the two CuOCu linkages apparently exert almost opposite contributions. On the phenolato side, the antiferromagnetic contribution may be expected to be intermediate between those occurring in **1** and **2** since CuOCu is 98.1° instead of 97.4° in **1** and 98.7° in **2**. The cyanato-*O* bridge appears to be at least as efficient as the azido one to favor a ferromagnetic interaction.

In the absence of additional experimental data, it does not seem reasonable to go farther in the interpretation of the magnetic properties. We may anticipate however that the angle between the plane of the bridging network and the group N_3^- or OCN^- plays an important role in the magnitude of the interaction. New results dealing with the same kinds of bridging networks will be presented in the near future.

Safety Notes. Perchlorate salts of metal complexes with organic ligands are potentially explosive. In general, when noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. If a perchlorate must be used, only small amounts of material should be prepared and this should be handled with great caution.

Registry No. **1**, 103001-54-3; **2**, 101661-17-0; **3**, 102920-55-8; 1,1-dimethylethylenediamine, 811-93-8; 2,6-diformyl-4-methylphenol, 7310-95-4.

Supplementary Material Available: Listings of atomic parameters for hydrogen atoms and anisotropic thermal parameters for non-hydrogen atoms (Tables XIII–XV) (3 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Rutgers,
The State University of New Jersey, New Brunswick, New Jersey 08903

Characterization of [*rac*-5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) 3-Sulfidopropionate Dimethanolate, $[Cu(tet\ b)SCH_2CH_2CO_2]\cdot 2CH_3OH$, a Stable Copper(II)–Aliphatic Thiolate Complex

Elizabeth John, Parimal K. Bharadwaj, Joseph A. Potenza,* and Harvey J. Schugar*

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The synthesis, X-ray structure, and preliminary electronic spectra of the title complex, the first stable Cu(II)–aliphatic thiolate compound, are presented. Crystals of $CuSO_2N_4C_{19}H_{40}\cdot 2CH_3OH$ are monoclinic, space group $P2_1/n$, with $a = 14.003$ (2) Å, $b = 13.683$ (2) Å, $c = 14.548$ (4) Å, $\beta = 91.85$ (2)°, $Z = 4$, and R_F (R_{wF}) = 0.051 (0.058) for 2276 reflections. The structure contains neutral Cu(II) monomers with distorted-trigonal-bipyramidal N_4S ligand donor sets. Equatorial ligation is provided by the sulfidopropionate S atom (Cu–S = 2.314 (2) Å) and two amine N atoms from the tet b ligand (Cu–N = 2.153 (4), 2.169 (4) Å), while two shorter axial Cu–N(tet b) bonds (2.031 (4), 2.001 (4) Å) complete the coordination. The macrocyclic tet b ligand is folded in its lowest energy conformation, and the carboxylate group is stabilized by hydrogen bonding to the tet b and solvate molecules. Electronic absorptions at ~27 800 and ~23 800 cm^{-1} are assigned as S → Cu(II) LMCT while additional spectral features in the 12 000–17 000-cm^{-1} range are assigned as ligand field transitions. Spectroscopic comparisons are presented between the title complex and a structurally similar Cu(tet b) complex of the aromatic thiolate *o*-sulfidobenzoate.

Introduction

The scope of stable Cu(II) aliphatic thiolate complexes has been limited to the type 1 sites in "blue" copper metalloproteins,[1] Cu(II)-doped liver alcohol dehydrogenase,[2] and the Cu_A site in cytochrome *c* oxidase.[3] There has been considerable interest in identifying the contributions of the Cu(II) aliphatic thiolate subunit of both biological and synthetic chromophores to their electronic spectral and vibrational features. While it has been clear for some time that the prominent absorption at ~16 000 cm^{-1} exhibited by type 1 Cu(II) systems must be due to σ(thiolate) → Cu(II) LMCT,[1] the identification and origins of the expected

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π(thiolate) → Cu(II) LMCT bands are not complete. Recent studies from the Solomon group indicate that the unpaired electron resides in an orbital that has considerably mixed Cu/S(thiolate) character.[4] Moreover, the results of their Xα calculations indicate that the prominent σ(thiolate) LMCT band should be flanked on either side by well-removed π(thiolate) LMCT bands, neither of which can originate from the sulfur 3s orbital, which is calculated to be ~7 eV more stable than the half-occupied HOMO. The availability of stable Cu(II) aliphatic thiolate complexes will facilitate experimental testing of these and other electronic structural predictions. The combined presence of LF absorptions, imidazole → Cu(II) LMCT absorptions, and the large UV absorption edge due to the aromatic amino acid residues complicate the electronic spectra of the type 1 Cu(II) chromophores and the ready identification of these π-symmetry thiolate LMCT bands; LMCT from the apically bound methionine sulfur is predicted and observed to be rather weak.[5-7] Also, interpretation of the type 1 chromophore vibrations that are in resonance with the prominent LMCT absorption[8-11] should be facilitated by spectroscopic studies of structurally defined Cu(II) aliphatic thiolates, particularly those that may be isotopically substituted at sulfur. The resonance Raman spectra of type 1 Cu chromophores differ more than the corresponding electronic spectra and thus have the potential of being a more sensitive probe of subtle structural differences.[12]

Despite the well-known redox instability of Cu(II) thiolate systems, we[12] and others[13-15] have been able to isolate and structurally characterize Cu(II) complexes that contain ligation by aromatic thiolates. However, electronic coupling between the thiolate sulfur 3p orbitals and the aromatic π systems[16] may result in spectroscopic complications not present for the aliphatic thiolate (cysteine) ligand in copper metalloproteins. It is possible to prepare stable synthetic Cu(II) aliphatic thiolate complexes, the first example of which is the subject of this report. The characterization of Cu(II) aliphatic dithiolate complexes that are potential models of the Cu$_A$ unit of cytochrome *c* oxidase[3] will be reported elsewhere.[17]

Experimental Section

1. Preparation of the Title Complex (1). The *dl* macrocyclic amine tet b was synthesized with use of a published procedure,[18] separated from the meso isomer tet a by fractional crystallization, and obtained in pure form as the monohydrate by recrystallization from water–ethanol (mp 98–107 °C, lit.[19] mp 97–105 °C). 3-Mercaptopropionic acid was obtained from the Aldrich Chemical Co. The acid was either used as received or converted to the crystalline and less pungent salt of dicyclohexylamine, which was prepared by mixing equimolar amounts of the acid and amine and then recrystallizing the resulting white mass from absolute ethanol (mp 124–128 °C). The title complex was prepared by reacting cold alkaline methanolic solutions of Cu(tet b)·SO$_4$ with 3-mercaptopropionate; vapor diffusion of ether caused the complex to precipitate as green crystals. In a typical experiment, a dark blue solution of Cu(tet b)·SO$_4$ was prepared by stirring a warm (~65 °C) mixture of 1 mmol of CuSO$_4$·5H$_2$O and 1.1 mmol of tet b in 8 mL of methanol. The solution was made alkaline with 2.6 mmol of KOH and filtered. The filtrate was combined with a solution of 1.3 mmol of 3-mercaptopropionic acid in 5 mL of methanol. Vapor diffusion of ether into the cold filtrate (6 °C) yielded green crystals after approximately 12 h. The green crystals deposited from blue solutions and yielded blue solutions when dissolved in methanol. The crystals are insoluble in water and unstable in air. The product was obtained in approximately 35% yield.

Table I. Crystal and Refinement Data for **1**

formula	CuSO$_2$N$_4$C$_{19}$H$_{40}$·2CH$_3$OH
fw	518.26
a, Å	14.003 (2)
b, Å	13.683 (2)
c, Å	14.548 (4)
β, deg	91.85 (2)
V, Å^3	2786 (2)
space group	$P2_1/n$
Z	4
no. of refs used to determine cell consts	25 (11.41 < θ < 15.20°)
d_{calcd}, g/cm^3	1.236
d_{obsd}, g/cm^3	1.23 (1)
λ(Mo Kα), Å	0.71073
monochromator	graphite
linear abs coeff, cm^{-1}	8.9
cryst dimens, mm	0.10 × 0.21 × 0.46
rel trans factor range	$0.91 < T < 1$
diffractometer	Enraf-Nonius CAD-4
data collection method	θ–2θ
2θ range, deg	$2 \leqslant 2\theta \leqslant 50$
temp, K	298 (1)
scan range, deg	0.90 + 0.35 tan θ
weighting scheme	$w = 4(F_o)^2/[\sigma(F_o)^2]^2$ [a]
no. of std reflecns	3
% variation in std intens	±0.1
no. of unique data collected	4877
no. of data used in refinement	2276 ($F_o^2 \geqslant 3\sigma(F_o^2)$)
data:parameter ratio	8.1
final GOF[b]	1.54
final R_F[c]	0.051
final R_{wF}[d]	0.058
systematic absences obsd	$0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$
final largest shift/esd	0.5
highest peak in final diff map, e/Å^3	0.54

[a] $[\sigma(F_o)^2]^2 = [S^2(C + R^2B) + (rF_o^2)^2]/(Lp)^2$, where S is the scan rate, C is the total integrated peak count, R is the ratio of scan to background counting time, B is the total background count, r is a factor introduced to downweight intense reflections, and Lp is the Lorentz–polarization factor. For the present structure, $r = 0.04$. [b] Error in an observation of unit weight, equal to $[\sum w(|F_o| - |F_c|)^2/(\mathrm{NO} - \mathrm{NV})]^{1/2}$, where NO is the number of observations and NV is the number of variables in the least-squares refinement. [c] $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $R_{wF} = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

2. Physical Measurements. Electronic spectra were recorded with a Cary Model 17 RI spectrophotometer. Samples were dispersed as KBr pellets or as mineral oil mulls. Room-temperature magnetic susceptibility data for **1** were obtained with a Cahn Faraday balance calibrated with Ni(en)$_3$·S$_2$O$_3$. Because of the instability of **1** in air, these measurements were made with use of suspensions of **1** in mineral oil. A suspension of **1** in ether was obtained by successive decantation of the original methanol/ether mother liquor followed by addition of fresh anhydrous ether. A suspension of approximately 3 mg of **1** in ether was added to a plastic capsule that contained 13 mg of mineral oil. Evaporation of the ether yielded the desired suspension of **1**, whose susceptibility was obtained

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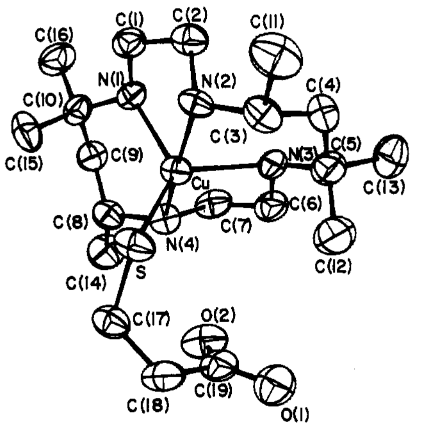

Figure 1. ORTEP view of the title complex **1** showing the atom-numbering scheme. Methanol solvate molecules [O(3)–C(20) and O(4)–C(21)] have been omitted for clarity.

after an additional correction was made for the diamagnetism of the mineral oil.

EPR spectra of polycrystalline **1** were measured with a Varian E-12 spectrometer calibrated with a Hewlett-Packard Model 5245-L frequency counter and a DPPH crystal ($g = 2.0036$). Crystals of **1** were protected from decomposition by a layer of dry ether.

3. X-ray Diffraction Studies. A crystal of **1** was mounted inside a glass capillary that contained a small amount of mother liquor well removed from the crystal. All diffraction measurements were made with an Enraf-Nonius CAD-4 diffractometer and graphite-monochromated Mo Kα radiation. The Enraf-Nonius Structure Determination Package[20] was used for data collection, processing, and structure solution. Crystal data and additional details of the data collection and refinement are presented in Table I. Intensity data were collected and corrected for decay, absorption (empirical), and Lp effects.

The structure was solved by direct methods[21] and refined on F with use of full-matrix least-squares techniques. An E map based on 350 phases from the starting set with the highest combined figure of merit revealed coordinates for Cu, S, and most of the tet b ligand atoms. The remaining non-hydrogen atoms were located from successive difference Fourier maps. At isotropic convergence, several H atoms were located on a difference map; coordinates for the remaining H atoms were calculated by assuming idealized bond geometry with C–H and N–H distances of 0.95 and 0.87 Å, respectively.[22] H atom temperature factors were set according to $B_H = B_n + 1$ where n is the atom bonded to H. Hydrogen atom parameters were not refined. Anisotropic refinement led to convergence with $R_F = 0.051$ and $R_{wF} = 0.058$. Final atomic parameters are listed in Table II, while a view of the structure is given in Figure 1. Lists of observed and calculated structure factors, anisotropic thermal parameters, and H atom coordinates are available.[23]

Results and Discussion

Description of the Structure. The structure contains discrete Cu(II) monomers with approximately trigonal-bipyramidal N_4S ligand donor sets. As indicated by the bond distances and angles in Table III, this coordination geometry is similar to that reported[12] for Cu(tet b)·(*o*-$SC_6H_4CO_2$) (**2**). In **1**, the tet b ligand is in its lowest energy folded configuration with both six-membered chelate rings in the chair and both five-membered chelate rings in the gauche conformation. Similar tet b conformations have been reported for **2**, for $[(\text{Cu tet b})_2\text{Cl}]^{2+}$, a dimeric complex with equivalent trigonal-bipyramidal N_4Cl donor sets,[24] and for two monomeric Cu(tet b)Y species, where Y = NO_3^-, OH_2.[25]

Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters for **1**

	x	y	z	B_{eq}, Å^2
Cu	0.13558 (6)	0.00833 (6)	0.16072 (6)	3.12 (2)
S	0.0647 (2)	0.1171 (2)	0.0576 (1)	4.04 (5)
O(1)	0.2785 (4)	0.3323 (4)	0.1096 (4)	5.9 (2)
O(2)	0.1913 (4)	0.2882 (4)	0.2283 (4)	5.5 (1)
O(3)	0.2912 (7)	0.3771 (8)	−0.0658 (6)	14.0 (3)
O(4)	0.213 (1)	0.559 (1)	−0.075 (1)	11.6 (5)
N(1)	0.0739 (4)	−0.1129 (4)	0.2321 (4)	3.2 (1)
N(2)	0.1506 (4)	−0.0899 (4)	0.0576 (4)	3.2 (1)
N(3)	0.2872 (4)	−0.0028 (5)	0.1945 (4)	3.4 (1)
N(4)	0.1324 (4)	0.0905 (4)	0.2744 (4)	3.3 (1)
C(1)	0.0621 (5)	−0.1910 (5)	0.1620 (5)	3.7 (2)
C(2)	0.1448 (5)	−0.1880 (5)	0.0993 (5)	3.7 (2)
C(3)	0.2324 (6)	−0.0736 (6)	−0.0027 (5)	3.9 (2)
C(4)	0.3286 (5)	−0.0793 (6)	0.0499 (6)	4.3 (2)
C(5)	0.3559 (5)	0.0005 (6)	0.1190 (5)	4.4 (2)
C(6)	0.3027 (6)	0.0668 (6)	0.2692 (5)	4.4 (2)
C(7)	0.2193 (6)	0.0671 (6)	0.3306 (5)	4.4 (2)
C(8)	0.0401 (6)	0.0882 (6)	0.3248 (5)	3.9 (2)
C(9)	0.0138 (6)	−0.0147 (6)	0.3577 (5)	4.2 (2)
C(10)	−0.0133 (5)	−0.0919 (5)	0.2846 (5)	3.5 (2)
C(11)	0.2306 (6)	−0.1431 (7)	−0.0853 (5)	5.4 (2)
C(12)	0.3500 (6)	0.1027 (6)	0.0713 (6)	5.4 (2)
C(13)	0.4601 (6)	−0.0183 (7)	0.1565 (7)	6.4 (3)
C(14)	0.0422 (7)	0.1599 (6)	0.4054 (6)	5.9 (2)
C(15)	−0.0937 (6)	−0.0543 (6)	0.2192 (6)	4.8 (2)
C(16)	−0.0480 (6)	−0.1822 (6)	0.3356 (6)	5.3 (2)
C(17)	0.0354 (6)	0.2372 (6)	0.1037 (5)	4.1 (2)
C(18)	0.1101 (6)	0.3143 (6)	0.0845 (6)	4.7 (2)
C(19)	0.2017 (6)	0.3100 (5)	0.1453 (6)	4.5 (2)
C(20)	0.277 (1)	0.291 (1)	−0.1354 (9)	16.2 (6)
C(21)	0.148 (2)	0.556 (2)	−0.128 (2)	11.4 (8)

The Cu–S bond length in **1** (2.314 (2) Å) is 0.045 (4) Å shorter than that reported for **2**. Both of these bond distances are substantially longer than that determined by single-crystal X-ray (2.13 Å) and EXAFS studies (2.08–2.10 Å)[26] for the Cu^{II}–S(cysteine) bond in plastocyanin, which contains distorted-tetrahedral CuN_2S(cysteine)S(methionine) units. Intermediate distances have been reported for the two Cu^{II}–S(cysteine) bonds (2.230 (5), 2.262 (4) Å) in the distorted-square-planar CuN_2S_2 unit of $Cu(SCH_2CH(CO_2CH_3)NHCH_2)_2$.[17] The observed Cu–S–C(17) bond angle in **1** (115.9 (2)°) is significantly larger than the corresponding values of 108.4 (4)° and 107° reported, respectively, for **2**[12] and plastocyanin.[6]

Equatorial Cu–N bond lengths in **1** (2.153 (4), 2.169 (4) Å) are significantly longer than the axial Cu–N bond lengths (2.031 (4), 2.001 (4) Å), a result that was also observed for **2**. The relationship of the Cu–N distances in several trigonal-bipyramidal CuN_4X complexes has been explored recently by using an angular overlap analysis,[27] which suggested that equatorial bond elongation in **2** was due to lack of π bonding with the saturated tet b ligand. As noted by a reviewer, some degree of trigonal compression appears to be commonplace for five-coordinate Cu(II) complexes whose geometries span the range between square pyramidal and trigonal bipyramidal.[28] These intermediate coordination geometries have been characterized by the structural index parameter $\tau = (\beta - \alpha)/60$, where β and α, respectively, are the largest and next largest metal–ligand bond angles in the complex.[28] For **1**, β corresponds to the N(2)–Cu–N(4) angle, which may be viewed either as defining the trigonal axis of a distorted trigonal bipyramid or constituting the greater basal angle of a distorted square pyramid. The apical ligand of this latter geometry would be N(3) with use of the criterion that it is the ligand not used to define β or α. These considerations applied to **1** and **2**, respectively, lead to τ values of (171.1° − 129.6°)/60° = 0.69 and (170.8° −

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Table III. Bond Distances (Å) and Angles (deg) in **1**

Cu–S	2.314 (2) [2.359 (4)][a]	N(4)–C(7)	1.478 (7)
Cu–N(1)	2.153 (4) [2.193 (10)]	N(4)–C(8)	1.508 (7)
Cu–N(2)	2.031 (4) [2.028 (9)]	C(1)–C(2)	1.498 (8)
Cu–N(3)	2.169 (4) [2.132 (9)]	C(3)–C(4)	1.529 (8)
Cu–N(4)	2.001 (4) [1.997 (10)]	C(3)–C(11)	1.532 (8)
S–C(17)	1.826 (6)	C(4)–C(5)	1.524 (8)
O(1)–C(19)	1.248 (7)	C(5)–C(12)	1.562 (8)
O(2)–C(19)	1.256 (7)	C(5)–C(13)	1.562 (8)
O(3)–C(20)[b]	1.566 (14)	C(6)–C(7)	1.493 (8)
O(4)–C(21)[b]	1.17 (2)	C(8)–C(9)	1.536 (8)
N(1)–C(1)	1.481 (7)	C(8)–C(14)	1.528 (8)
N(1)–C(10)	1.491 (7)	C(9)–C(10)	1.537 (7)
N(2)–C(2)	1.476 (7)	C(10)–C(15)	1.539 (8)
N(2)–C(3)	1.482 (7)	C(10)–C(16)	1.528 (8)
N(3)–C(5)	1.485 (7)	C(17)–C(18)	1.518 (8)
N(3)–C(6)	1.455 (7)	C(18)–C(19)	1.535 (8)
S–Cu–N(1)	129.6 (1) [120.8 (3)]	N(2)–C(3)–C(11)	112.2 (5)
S–Cu–N(2)	90.0 (1) [90.9 (3)]	C(4)–C(3)–C(11)	110.7 (5)
S–Cu–N(3)	126.0 (1) [135.4 (3)]	C(3)–C(4)–C(5)	119.5 (5)
S–Cu–N(4)	98.9 (1) [98.0 (3)]	N(3)–C(5)–C(4)	108.2 (5)
N(1)–Cu–N(2)	84.2 (2) [89.2 (4)]	N(3)–C(5)–C(12)	109.2 (5)
N(1)–Cu–N(3)	104.0 (2) [103.5 (4)]	N(3)–C(5)–C(13)	110.9 (5)
N(1)–Cu–N(4)	90.8 (2) [84.4 (4)]	C(4)–C(5)–C(12)	109.8 (5)
N(2)–Cu–N(3)	89.8 (2) [84.3 (4)]	C(4)–C(5)–C(13)	108.9 (5)
N(2)–Cu–N(4)	171.1 (2) [170.8 (4)]	C(12)–C(5)–C(13)	109.8 (5)
N(3)–Cu–N(4)	84.2 (2) [90.7 (4)]	N(3)–C(6)–C(7)	110.4 (5)
Cu–S–C(17)	115.9 (2) [108.4 (4)]	N(4)–C(7)–C(6)	108.4 (5)
Cu–N(1)–C(1)	105.2 (3) [103.1 (7)]	N(4)–C(8)–C(9)	112.8 (5)
Cu–N(1)–C(10)	116.5 (3) [119.6 (8)]	N(4)–C(8)C(14)	111.4 (5)
C(1)–N(1)–C(10)	114.6 (4)	C(9)–C(8)–C(14)	110.4 (5)
Cu–N(2)–C(2)	106.8 (3) [108.0 (7)]	C(8)–C(9)–C(10)	118.1 (5)
Cu–N(2)–C(3)	116.0 (3) [115.3 (7)]	N(1)–C(10)–C(9)	107.4 (5)
C(2)–N(2)–C(3)	115.7 (4)	N(1)–C(10)–C(15)	110.1 (5)
Cu–N(3)–C(5)	118.9 (3) [119.5 (7)]	N(1)–C(10)–C(16)	111.8 (5)
Cu–N(3)–C(6)	104.1 (3) [105.7 (7)]	C(9)–C(10)–C(15)	111.0 (5)
C(5)–N(3)–C(6)	116.7 (5)	C(9)–C(10)–C(16)	107.2 (5)
Cu–N(4)–C(7)	107.2 (4) [107.7 (7)]	C(15)–C(10)–C(16)	109.4 (5)
Cu–N(4)–C(8)	115.7 (3) [115.4 (8)]	S–C(17)–C(18)	113.2 (5)
C(7)–N(4)–C(8)	115.4 (4)	C(17)–C(18)–C(19)	115.8 (5)
N(1)–C(1)–C(2)	109.2 (5)	O(1)–C(19)–O(2)	125.9 (7)
N(2)–C(2)–C(1)	109.2 (5)	O(1)–C(19)–C(18)	117.8 (6)
N(2)–C(3)–C(4)	112.5 (5)	O(2)–C(19)–C(18)	116.2 (7)

[a] Values in brackets are corresponding parameters for Cu(tet b)(*o*-$SC_6H_4CO_2$) taken from ref 12. [b] Atoms O(3), C(20), O(4), and C(21) correspond to the methanol solvate molecules.

Table IV. Least-Squares Planes[a]

plane I		plane II		plane III		plane IV	
N(1)*	0.000	N(1)*	0.000	N(2)*	−0.013 (5)	N(1)*	−0.010 (5)
N(3)*	0.000	N(2)*	0.000	N(3)*	0.013 (5)	N(4)*	0.010 (5)
S*	0.000	N(4)*	0.000	C(3)*	0.015 (7)	C(8)*	−0.012 (6)
Cu	−0.074 (1)	Cu	0.135 (1)	C(5)*	−0.015 (7)	C(10)*	0.012 (6)
N(2)	1.952 (5)	N(3)	−1.932 (5)	Cu	0.953 (1)	Cu	0.979 (1)
N(4)	−2.054 (5)	S	1.988 (2)	C(4)	−0.664 (7)	C(9)	−0.688 (6)

[a] Starred atoms were used to define the plane. Displacement of atoms from the mean plane is given in Å.

Table V. Possible Hydrogen-Bonding Contacts in **1**

donor (D)	hydrogen (H)	acceptor (A)	D–H···A, deg	D···A, Å	H···A, Å	D–H, Å
N	H(N1)	O(1)^{i}[a]	167	3.136 (6)	2.28	0.87
N	H(N3)	O(2)^{i}	163	3.085 (6)	2.22	0.89
N	H(N4)	O(2)^{ii}	156	2.913 (6)	2.07	0.89
O	H(O3)	O(1)^{ii}	97	2.640 (9)	2.34	0.96
O	H(O3)	O(4)^{ii}	94	2.74 (2)	2.51	0.96

[a] Symmetry transformations: i = $^1/_2 - x, y - {}^1/_2, {}^1/_2 - z$; ii = x, y, z.

135.4°)/60° = 0.59. This analysis suggests that **1** lies closer to the idealized trigonal-bipyramidal limit (τ = 1.0) than the square-pyramidal limit (τ = 0). Possible electronic spectroscopic implications of complex **2** having more square-pyramidal character are considered in the next section.

As shown in Table IV, the Cu atom deviates 0.074 (1) Å from the plane defined by the equatorial ligation N(1)–S–N(3) toward N(4) and 0.135 (1) Å from the N(1)–N(2)–N(4) plane toward the S atom. The latter deviation is approximately 4 times larger than that observed for **2** (0.032 Å). Neither the carboxylate nor the methanol solvate O atoms are bound to Cu, as indicated by the Cu···O separations, the shortest of which, Cu···O(2), is 4.023 (4) Å. Finally, we note that the O and N atoms are involved in several intra- and intermolecular hydrogen bonds (Table V), which help fix the orientation of the carboxylate group with respect to the C(17)–C(18)–C(19) plane.

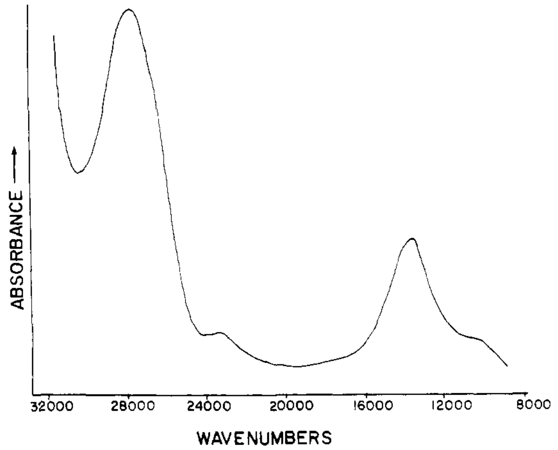

Figure 2. Electronic spectrum of **1** obtained as a mineral oil mull at 298 K.

Electronic Structural Aspects of 1. The corrected magnetic moment of **1** at 298 K is 1.4 (2) μ_B.[29] Owing to instability of the dry complex, susceptibility studies were performed on crystals protected from drying by mineral oil (see Experimental Section). The observed value of ~1.4 μ_B was reproducible (five trials) and probably arises from an overestimate of the sample weight due to incomplete evaporation of the ether transfer solvent. In view of the EPR and electronic spectral results presented below, we do not attribute any significance to the result that the measured magnetic moment of **1** falls below the range observed for magnetically dilute five-coordinate Cu(II) complexes.[30]

Mull spectra of **1** (Figure 2) contain a broad, prominent absorption at ~13 800 cm^{-1} flanked by a weaker band at lower energy (~11 600 cm^{-1}). These spectral features are characteristic of approximately trigonal-bipyramidal $Cu^{II}N_4X$ complexes, where X = $^-SC_6H_4CO_2^-$, Cl^-, CN^-.[11] Green crystals of **1** are soluble in water and methanol and insoluble in common organic solvents such as acetonitrile, acetone, methylene chloride, etc. Methanolic solutions of **1** are initially green and rapidly (seconds) turn blue. The prominent near-UV feature at ~27 800 cm^{-1} is not exhibited by the blue solution species. EPR studies of glassed methanolic **1** at 80 K reveal that two tetragonal Cu(II) species having different $A_{\parallel}$ values are present in about equal amounts. Presumably, the solution equilibria are such that the mercaptopropionate ligand is displaced by solvent. Attempts to reduce ligand displacement by increasing the mercaptopropionate concentration by a factor of 1.5 were not successful, while higher mercaptopropionate levels resulted in redox decomposition of the solution Cu(II) species. EPR spectra of polycrystalline **1** are rhombic in appearance; the observed g values at 80 K are 2.047, ~2.07 (poorly resolved), and 2.163. Comparably appearing crystal spectra and g values (2.074, 2.086 (poorly resolved), 2.117) are exhibited by **2**.[12] Owing to the difficulty of obtaining single crystals of either **1** or **2** larger than ~0.2 mm in length, molecular g values of these complexes have not been obtained.

The prominent absorption of **1** at ~27 000 cm^{-1} and the weaker flanking absorption at ~23 800 cm^{-1} are too high in energy for ligand field absorptions of Cu(II) and too low in energy to be N → Cu(II) LMCT absorptions originating from a secondary aliphatic amine.[31] The structurally related complex Cu(tet b)-$SC_6H_4CO_2$ (**2**) exhibits a prominent absorption at 27 800 cm^{-1} that was assigned as σ(thiolate) → Cu(II) LMCT,[12] and a similar assignment for the corresponding absorption of **1** is proposed here. However, the weaker flanking LMCT absorption of complex **2** is unmistakably split into overlapping absorptions at ~23 900 and ~23 300 cm^{-1}. These latter absorptions were assigned as π(thiolate) → Cu(II) LMCT absorptions from approximately degenerate sulfur valence orbitals. This assignment is not consistent with the results of recent Xα calculations, which have yielded a detailed picture of the valence orbitals of coordinated thiolate.[4] Because the S 3s orbital is unexpectedly stable and effectively corelike in nature, the thiolate valence orbitals have relatively little S 3s character. The three valence orbitals of coordinated thiolate exhibit appreciable metal character in the three- and four-coordinate model Cu(II) sites treated by the calculations. The "lone pairs" of the ligated thiolate consist of a σ-symmetry thiolate valence orbital flanked at higher and lower energy by π-symmetry thiolate valence orbitals that have considerable Cu 3d and alkyl character, respectively. Considering the trigonal-bipyramidal CuN_4S chromophores present in **1** and **2**, it seems that the prominent σ(thiolate) LMCT absorption at ~28 000 cm^{-1} should be flanked by only a *single* LMCT absorption at lower energy; the other π(thiolate) LMCT absorption should lie toward higher energy. This expectation has been realized only for complex **1**.

In addition to being split, the absorptions of **2** at ~24 000 cm^{-1} are apparently more intense than the single absorption of **1** at this energy. Although the instability of **1** in solution makes a quantitative comparison impossible, the 24 000-cm^{-1} absorption in the mull spectra of **1** is weaker than the LF absorptions whereas the reverse is true for **2**. A reviewer has suggested two possible reasons for the higher intensity of the LMCT absorption at ~24 000 cm^{-1} observed for **2**. First, the structural index parameter analysis described above indicates the Cu(II) d vacancy of **2** has more $d_{x^2-y^2}$ character. This would allow better overlap with the thiolate sulfur orbitals and presumably would enhance thiolate → Cu(II) LMCT absorption. Moreover, the greater polarizability of the aromatic thiolate might also enhance the Cu(II)–thiolate interaction and result in increased LMCT band intensity relative to that observed for the aliphatic thiolate analogue. Finally, the "extra" low-energy LMCT exhibited by **2** in our view suggests that an additional LMCT pathway may be occurring. One possibility for such a pathway is *outer-sphere* thiolate LMCT transmitted via the *o*-carboxylate group that participates in intramolecular and intermolecular hydrogen-bonding interactions with three of the tet b amine groups. The lack of detectable "extra" LMCT associated with the similar hydrogen-bonding pathway present in **1** may be due to poor coupling of the thiolate and carboxylate groups via the saturated CH_2CH_2 fragment. There is precedent for antiferromagnetic coupling of Cu(II) ions via hydrogen bond exchange pathways.[32,33] We have attempted to detect the presence of outer-sphere LMCT by preparing a complex of Cu(tet b)$^{2+}$ with the dianion of (*o*-mercaptophenyl)acetate.[34] The aromatic thiolate and aliphatic carboxylate are decoupled in this latter ligand by the intervening CH_2 group. Unfortunately, the desired complex is redox-unstable, and only brown decomposition products could be isolated.

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Supplementary Material Available: Listings of anisotropic thermal parameters and hydrogen atom coordinates (2 pages). Ordering information is given on any current masthead page.

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(29) The reported magnetic moment includes a diamagnetic correction of -332×10^{-6} cgsu (per Cu), which has been calculated from Pascal's constants.

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