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Coordination Chemistry of New Sulfur-Containing Ligands. 17. Preparation, Characterization, and Crystal and Molecular Structure of [*N*,*N*′-Trimethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylato)]copper(II), a Highly Distorted CuN_2S_2 Compound[1]

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The copper(II) complex of the N_2S_2 tetradentate ligand *N*,*N*′-trimethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) was prepared by reaction of the neutral ligand with an equivalent amount of copper acetate in methanol. A low-energy, broad, and asymmetric absorption band at 10.5 cm^{-1} in the electronic spectrum, coupled with the observed electron spin resonance parameters ($A_{\|} = 160$ G, $g_{\|} = 2.132$, $A_0 = 67.9$ G, $g_0 = 2.060$), suggests a copper(II) coordination site intermediate between planar and pseudotetrahedral geometry. Since the recent structural results of the type I copper(II)-containing metalloenzyme plastocyanim indicates a distorted N_2S_2 coordination,[21] the further structural study of this compound is warranted. The crystal and molecular structure of the title compound was solved at 24 ± 1 °C by a single-crystal X-ray diffraction study. The complex crystallizes in the centrosymmetric monoclinic space $C2/c$ with $a = 16.7219$ (17) Å, $b = 8.4009$ (7) Å, $c = 14.5507$ (16) Å, $\beta = 108.337$ (8)°, $V = 1940.3$ Å^3, ρ(obsd) 1.54 g cm^{-3}, and ρ(calcd) = 1.53 g cm^{-3} for mol wt 448.2 and $Z = 4$. Diffraction data were collected with a Syntex $P2_1$ automated diffractometer using graphite-monochromatized Mo Kα radiation. The copper and two sulfur atoms were located in a Patterson synthesis; all other nonhydrogen atoms were located via difference Fourier techniques, and hydrogen atoms were placed in calculated positions. Final refinement resulted in discrepancy indices of $R_F = 4.31\%$ and $R_{wF} = 4.42\%$ for all 1273 symmetry-independent reflections with $4° \leq 2\theta \leq 45°$ (none rejected). The molecules are monomeric, are well separated, and lie on a C_2 axis. The copper–sulfur distance is 2.2225 (11) Å and the copper–nitrogen distance is 1.9498 (30) Å. Bond distances in the five-membered chelate ring indicate that a great deal of π delocalization exists. The plane defined by the copper and two ligand sulfur atoms intersects the plane defined by the copper and two nitrogen atoms, forming a dihedral angle of 53° (90° would be ideal for a C_{2v} inner coordination sphere geometry while 0° would be ideal for planar geometry) indicating the extent of distortion in the inner coordination sphere. The spectral properties of the copper(II) atom are discussed in terms of the geometry and the ligand atom type.

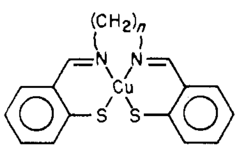
Introduction

Recent interest in our laboratories, and others, has centered on the design, preparation, and characterization of small-molecule complexes of copper(II) which offer insight into the coordination chemistry of copper(II) in metalloproteins. One of the most exciting synthetic challenges in recent years has been to prepare complexes which mimic spectral properties of the "blue" copper(II) (type I) site in proteins such as laccase, plastocyanin, stellacyanin, ceruloplasmin, and ascorbate oxidase.[3-8] Such authentic synthetic analogues would be invaluable to the understanding of the detailed stereoelectronic properties of copper(II) in this environment. Various coordination sites have been proposed for these copper(II) sites.[9-20] They have in common a geometry intermediate between tetrahedral and square planar with two nitrogen ligand atoms (imidazole nitrogen atoms from histidine residues) and at least one sulfur ligand atom (thiolate group from a cysteine residue). The recent X-ray structure of plastocyanin to 2.7-Å resolution indicates an N_2S_2 coordination for copper(II) with the second sulfur ligand atom derived from a methionine residue.[21] Other "blue" copper(II) proteins, such as stellacyanin,[22] contain no methionine residues, so other ligand atoms such as nitrogen or oxygen are still possible. Regardless, we feel that any distorted pseudotetrahedral copper(II) complex, where detailed spectral and structural data are available, is useful for providing the data base for understanding the various type I copper(II) centers.

Relatively few CuN_3S and CuN_2S_2 compounds which are severely distorted from the normally planar configuration found for copper(II) systems have been reported. Spectral data of a CuN_3S species with tris(pyrazolyl) borate serving as the nitrogen ligand and ethyl cysteinate or *p*-nitrobenzenethiolate as the sulfur ligand have been interpreted in terms of a pseudotetrahedral geometry.[23] These complexes, unfortunately, were not stable above −30 °C. Schugar and coworkers[24] have reported a nearly "tetrahedral" CoN_2S_2 complex which was valuable in the interpretation of Co(II)-substituted type I copper(II) sites.

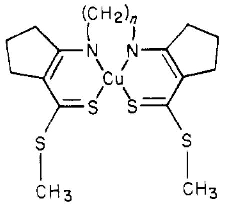
We have exploited the utility of sulfur-containing Schiff-base ligands to prepare "distorted" copper(II) complexes.[25,26]

Corrigan and co-workers[27] have recently reported the spectral properties of the CuN_2S_2 chromophores in the tetradentate mercaptobenzaldimine complexes I. They also reported



I: $n = 2, 3$

preliminary structural data for the $n = 2$ complex, but the spectral properties of that complex were not similar to type I centers. We have prepared the ligand II by employing the



II

method recently reported by Bordas et al.[28a] and Mondal et al.[28b] in the hope that the $(CH_2)_3$ backbone would distort the coordination geometry from a square-planar configuration toward a tetrahedral configuration. The results of this study are reported here.

Experimental Section

Materials. All reagents and solvents were commercially obtained, were of reagent grade, and were used without further purification.

Synthesis. The ligand *N,N'*-trimethylenebis(methyl 2-amino-1-cyclopentenedithiocarboxylate) was prepared by the method of Bordas et al.[28a] with 1,3-diaminopropane used in place of ethylenediamine. The thermal instability of the starting material, ammonium 2-amino-1-cyclopentenedithiocarboxylate, was overcome by a later method[29] (yield ~70%).

The copper(II) complex was prepared in methanol by the method of Mondal et al.[28b] The complex was isolated as a dark brown solid (yield ~40%). Anal. Calcd for $C_{17}H_{24}N_2S_4Cu$: C, 45.56; H, 5.40; N, 6.25. Found (Atlantic Microlab, Inc., Atlanta, GA): C, 45.70; H, 5.54; N, 6.20. Crystals suitable for the single-crystal X-ray diffraction study were obtained by slow evaporation of a saturated methylene chloride solution.

Physical Measurements. Electron spin resonance spectra were obtained at 120 and 300 K with a Varian E-9 spectrometer operating near 9 GHz (X-band). Spectra were obtained in a 50/50 (by volume) *N,N*-dimethylformamide/methylene chloride glass (120 K) and in solution (300 K). The spin Hamiltonian parameters were calculated as previously reported.[30] Optical spectra were determined at room temperature in both methylene chloride and *N,N*-dimethylformamide with a Cary 14 spectrophotometer.

Crystal Data Collection. The crystal used in the diffraction experiment was an irregularly shaped rectangular prism measuring approximately 0.25 mm × 0.21 mm × 0.20 mm. The crystal was jammed into a 0.2-mm thin-walled capillary which was sealed and fixed with beeswax into an aluminum pin on an eucentric goniometer head. The goniometer head was fixed to the goniostat, and the crystal was centered in the X-ray beam of a Syntex $P2_1$ four-circle diffractometer under control of a Data General Nova 1200 computer with 24K of 16-bit word memory and a Diablo disk unit of 1.2 million 16-bit words. The relative orientation and unit cell parameters of the crystal were determined, and the X-ray data were collected by methods described previously.[31] The crystal was found to possess monoclinic symmetry. Inspection of the collected data revealed the systematic absences hkl for $h + k = 2n + 1$ and $h0l$ for $l = 2n + 1$. Possible space groups are the centrosymmetric monoclinic space group $C2/c$ [C_{2h}^6; No. 15] or the noncentrosymmetric space group Cc [C_s^4; No. 9]. The former was indicated by intensity statistics and confirmed by the successful solution of the crystal structure. Specifics for data collection are given in Table I.

Table I. Data for the X-Ray Diffraction Study of $Cu(S_4N_2C_{17}H_{24})$

(A) Crystal Data

cryst system: monoclinic
space group $C2/c$ [C_{2h}^6; No. 15]
$a = 16.7219\ (17)$ Å
$b = 8.4009\ (7)$ Å
$c = 14.5507\ (16)$ Å
$\beta = 108.337\ (8)^\circ$
$V = 1940.3$ Å^3
$T = 24 \pm 1$ °C
$Z = 4$
mol wt 448.2
ρ(obsd) = 1.54 g/cm^3 [a]
ρ(calcd) = 1.53 g/cm^3

(B) Intensity Data

radiation: Mo Kα
monochromator: highly oriented graphite
rflcns measd: $h,k,\pm l$
max 2θ: 45°
min 2θ: 4°
scan type: θ–2θ
scan speed: 4°/min
scan range: sym, $[1.8 + \Delta(\alpha_2 - \alpha_1)]^\circ$
rflcns collected: 1273
abs coeff: 15.8 cm^{-1}; empirical abs cor made, based on series of ψ scans

[a] Measured by neutral buoyancy in saturated aqueous KI.

Solution and Refinement of the Structure

Initial calculations, through the generation of a Patterson synthesis, were performed by using the Syntex XTL structure determination system, including the aforementioned computing hardware and a locally modified version of the XLT conversational crystallographic program package. Subsequent difference Fourier syntheses and structure refinement were carried out on the CDC 6600/CYBER 173 computer at the State University of New York at Buffalo. Programs other than those in the Syntex XTL structure determination system: TAPRE (reads nine-track, ASCII-character string magnetic tape created by the program CDCOUT of the XLT system and converts the tapes read to coded files); JIMDAP (Fourier synthesis, derived from A. Zalkin's FORDAP) by J. A. Ibers and co-workers; LSHF (structure factor calculations and full-matrix least-squares refinement), STAN1 (distances and angles and their esd's), and PLOD (least-squares planes) all by B. G. DeBoer; ORTEP-II (thermal ellipsoid plots) by C. K. Johnson.

Scattering factors for neutral copper, sulfur, nitrogen, and carbon were taken from the compilation of Cromer and Waber;[32] for hydrogen, the "best floated spherical H atom" values of Stewart et al.[33] were used. Both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all nonhydrogen atoms by using the values of Cromer and Liberman.[34]

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where $w = [\sigma(|F_o|)]^{-2}$. Discrepancy indices used in the text are defined in eq 1 and 2. The "goodness of fit" (GOF) is defined by eq 3, wherein NO is the number of observations and NV is the number of variables.

$$R_F = \left[\frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \right] \times 100\ (\%) \tag{1}$$

$$R_{wF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} \times 100\ (\%) \tag{2}$$

$$\mathrm{GOF} = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\mathrm{NO} - \mathrm{NV}} \right]^{1/2} \tag{3}$$

The positions of the copper atom and the two sulfur atoms were determined from a three-dimensional Patterson synthesis. Subsequent least-squares refinement and difference Fourier maps allowed the location of all carbon and nitrogen atoms of the ligands. Positions of all hydrogen atoms were calculated, and shifts in their positional parameters were constrained to be equal to those of the appropriate bonded carbon atom (i.e., each CH system was treated as a rigid nonrotating group). There was evidence for secondary extinction, and a correction was made,[35] the final value of c being 0.131×10^{-6}. Final convergence was reached with $R_F = 4.31\%$, $R_{wF} = 4.42\%$, and GOF = 1.843. The highest feature on a final difference Fourier synthesis was a peak of height 0.68 e Å^{-3} at the position 0.104, 0.246, –0.165. The structural analysis is thus both correct and complete.

Table II. Positional Parameters and Their Standard Deviations for $Cu(S_4N_2C_{17}H_{24})$

atom	x	y	z
Cu[a]	0.00000	0.50603 (8)	0.25000
S(1)	0.08591 (7)	0.32445 (12)	0.22141 (8)
S(2)	0.19696 (8)	0.27217 (18)	0.09987 (10)
N	0.01030 (20)	0.66560 (36)	0.15707 (24)
C(1)	0.2264 (3)	0.1225 (7)	0.1886 (4)
C(2)	0.1267 (2)	0.3981 (5)	0.1350 (3)
C(3)	0.1111 (2)	0.5409 (5)	0.0889 (3)
C(4)	0.0568 (2)	0.6661 (5)	0.0995 (3)
C(5)	0.0603 (3)	0.8025 (5)	0.0332 (3)
C(6)	0.1382 (3)	0.7688 (6)	0.0031 (4)
C(7)	0.1512 (3)	0.5900 (6)	0.0125 (3)
C(8)	0.0422 (3)	0.8082 (5)	0.3394 (4)
C(9)[a]	0.0000	0.9067 (7)	0.2500
H(1C1)	0.2645	0.0496	0.1746
H(2C1)	0.2524	0.1700	0.2500
H(3C1)	0.1770	0.0676	0.1895
H(1C5)	0.0661	0.9010	0.0667
H(2C5)	0.0111	0.8050	−0.0217
H(1C6)	0.1858	0.8231	0.0444
H(2C6)	0.1290	0.8012	−0.0619
H(1C7)	0.2095	0.5648	0.0332
H(2C7)	0.1243	0.5386	−0.0474
H(1C8)	0.0984	0.8300	0.3782
H(2C8)	0.0101	0.7764	0.3798
H(1C9)	0.0420	0.9720	0.2379

[a] Occupancy 0.5 for calculations.

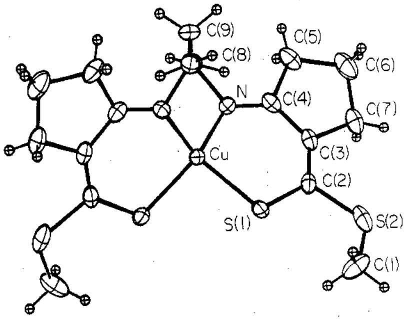


Figure 1. ORTEP-II diagram of $Cu(S_4N_2C_{17}H_{24})$; 30% probability ellipsoids. The C_2 axis passes through C(9) and Cu.

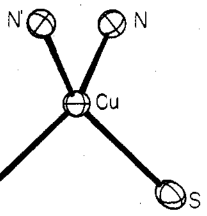


Figure 2. ORTEP-II diagram of CuN_2S_2 core: CuSS′ plane is that of the paper.

Positional parameters are collected in Table II; thermal parameters are presented in Table III.

Results and Discussion

The characterization and explanation of the stereoelectronic properties of Cu(II) complexes involving sulfur ligation are important when we consider the intense interest involving type I copper(II) coordination in proteins. Despite this interest, relatively few copper(II)–mercaptide complexes are known, and especially few distorted copper(II) complexes with any sulfur ligating groups have been reported. Attempts to prepare such systems invariably result in reduction of the Cu(II) to Cu(I) or are stable only at low temperatures. A few incompletely characterized products prepared from the reaction of copper(II) with thiol- and imidazole-containing peptides have recently been proposed as type I models.[36]

In an effort to overcome the problems of metal reduction and thermal instability and yet characterize copper(II) coordination complexes, we have considered forms of sulfur ligation other than copper(II)–thiol.

Synthesis and Spectral Properties

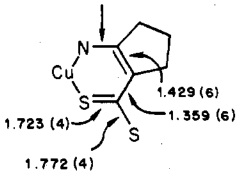
We, as well as others, have recently reported the preparation of copper(II) complexes having an N_2S_2 coordination donor set.[25,26,37,38] In each case the sulfur ligand atom has been of the thioketonate (=S–M) type rather than thiolate (–S–M) or thioether (>S–M) type. The tetradentate Schiff base, N_2S_2, ligands we particularly considered were derived from aliphatic diamines. By increasing the length of the diamine bridge it was possible to produce a ligand in which the four donor atoms might no longer settle into a planar coordination environment. Spectral data of these systems indicate that a distortion does occur.[26] Normally, a red shift in the d–d band and a decrease in the magnitude of the A_{zz} and A_0 spin Hamiltonian parameters were observed as the $(CH_2)_n$ backbone was lengthened. In the case under investigation here, we were able to isolate single crystals of what was expected to be a rather distorted CuN_2S_2 complex.

Mondal et al. have noted that the visible electronic spectrum of the CuN_2S_2 complex of II where $n = 2$ contained a broad band centered at 12.3 $cm^{-1} \times 10^3$. For the CuN_2S_2 complex of II where $n = 3$, we observe a similar band centered at 10.5 $cm^{-1} \times 10^3$. It is clear that a distinctive red shift has occurred as expected for any transition-metal complex where the ligands are unchanged but the coordination geometry is changed from a pseudo-square-planar to a pseudotetrahedral geometry. The electron spin resonance parameters for the three-carbon-bridged complex are $A_{\|} = 160$ G, $g_{\|} = 2.132$, $A_0 = 67.9$ G, $g_0 = 2.060$, $A_{\perp}(\text{calcd}) = 21.9$, and $g_{\perp}(\text{calcd}) = 2.024$. These values are consistent with neither square-planar nor pure tetrahedral geometry. They are, however, similar to other CuN_2S_2 complexes with a three-carbon-atom bridge characterized in our laboratories[26] and suggest a copper(II) environment intermediate between the two extreme coordination geometries.

Description of Structure

The structure of this CuN_2S_2 complex consists of discrete, well-separated monomers with a distorted inner coordination sphere. The molecules have crystallographically dictated C_2 (2) symmetry. An ORTEP diagram, which indicates the labeling of atoms, is shown in Figure 1. Tables IV and V list the bond distances and bond angles in the complex. The Cu–S and Cu–N distances are normal. The distortion of the inner coordination sphere can be recognized by determining the angle between the planes formed by the CuN_2 atoms and the CuS_2 atoms. Table VI shows the planes calculated for these two groups of three atoms. The angle of intersection of the planes is 52.8°. Clearly an angle of 90° would represent the maximum distortion of the inner-sphere atoms and 0° would represent a planar situation. We can find no other examples in the literature of a sulfur-containing soluble copper(II) *complex* which shows such a distortion.

The ligand bond distances within the six-membered coordination ring are shown below with the formal Lewis structure.



The formal C–C double bond in this chelate ring is longer than the formal C–C or C–N single bond. A great deal of resonance π delocalization must exist in the ring. This effect can

Table III. Thermal Parameters and Their Standard Deviations for $Cu(S_4N_2C_{17}H_{24})^{a,b}$

atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	3.39 (4)	2.42 (3)	3.93 (4)	0.00	2.18 (3)	0.00
S(1)	4.30 (5)	2.96 (5)	4.57 (5)	0.75 (4)	2.71 (4)	0.43 (4)
S(2)	5.11 (7)	7.26 (8)	6.00 (7)	1.80 (6)	3.41 (6)	−0.41 (6)
N	3.56 (16)	2.64 (15)	4.51 (17)	0.41 (12)	2.00 (14)	0.98 (13)
C(1)	5.01 (26)	6.36 (30)	7.84 (32)	2.64 (23)	1.66 (23)	−1.17 (26)
C(2)	2.75 (18)	4.14 (22)	3.62 (19)	−0.10 (16)	1.67 (15)	−0.60 (17)
C(3)	3.06 (19)	4.55 (23)	3.16 (18)	−0.74 (16)	1.47 (15)	−0.04 (17)
C(4)	3.00 (19)	3.79 (20)	3.53 (19)	−0.93 (16)	0.86 (16)	0.20 (16)
C(5)	4.67 (24)	4.72 (24)	4.54 (23)	−1.18 (19)	1.35 (19)	1.33 (19)
C(6)	7.22 (32)	6.95 (32)	5.06 (27)	−2.42 (26)	3.34 (24)	0.27 (23)
C(7)	4.80 (24)	6.67 (30)	4.57 (23)	−1.29 (22)	2.83 (20)	0.23 (22)
C(8)	4.15 (22)	3.81 (23)	7.70 (30)	−1.80 (18)	2.95 (22)	−1.20 (22)
C(9)	6.78 (42)	2.26 (28)	10.47 (55)	0.00	5.23 (41)	0.00

atom	B_{iso}, Å^2	atom	B_{iso}, Å^2	atom	B_{iso}, Å^2	atom	B_{iso}, Å^2
H(1C1)	7.46	H(1C5)	5.56	H(2C6)	7.00	H(1C8)	5.85
H(2C1)	7.46	H(2C5)	5.56	H(1C7)	5.90	H(2C8)	5.85
H(3C1)	7.46	H(1C6)	7.00	H(2C7)	5.90	H(1C9)	6.68

[a] The anisotropic thermal parameter is defined by the expression $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{12}hla^*c^* + 2B_{23}klb^*c^*)]$. [b] Isotropic thermal parameters are given for hydrogen atoms. These are based on the *isotropic* thermal parameters of the attached carbon atoms: $B(H_i) = B(C_i) + 1.0$ (Å^2).

Table IV. Bond Distances (Å) for $Cu(S_4N_2C_{17}H_{24})$

Cu–S	2.2225 (11)	C(3)–C(4)	1.4291 (56)
Cu–N	1.9498 (30)	C(7)–C(6)	1.5179 (69)
C(1)–S(2)	1.7573 (55)	C(6)–C(5)	1.5255 (63)
C(2)–S(1)	1.7225 (38)	C(5)–C(4)	1.5104 (54)
C(2)–S(2)	1.7716 (38)	C(4)–N	1.3097 (47)
C(2)–C(3)	1.3592 (57)	N–C(8)	1.4954 (48)
C(3)–C(7)	1.5259 (52)	C(8)–C(9)	1.5157 (57)

Table V. Bond Angles (deg) for $Cu(S_4N_2C_{17}H_{24})^a$

(A) Angles within the CuN_2S_2 Core			
S(1)–Cu–S(1)′	93.32 (6)	N–Cu–N′	93.13 (19)
S(1)–Cu–N	97.98 (9)	S–Cu–N′	143.61 (10)
(B) Angles Involving Ligating Atoms at Vertex and Copper			
Cu–S(1)–C (2)	108.53 (15)	Cu–N–C (8)	110.28 (24)
Cu–N–C (4)	130.20 (28)		
(C) Angles within the Ligand			
C(1)–S(2)–C(2)	105.85 (20)	C(6)–C(5)–C(4)	104.55 (38)
S(1)–C(2)–S(2)	116.57 (24)	C(5)–C(4)–C(3)	109.63 (34)
S(1)–C(2)–C(3)	128.17 (31)	C(5)–C(4)–N	124.14 (38)
C(2)–C(3)–C(4)	128.83 (35)	C(3)–C(4)–N	126.23 (36)
C(2)–C(3)–C(7)	122.55 (39)	C(4)–N–C(8)	119.44 (33)
C(3)–C(7)–C(6)	104.46 (38)	C(8)–C(9)–C(8)′	113.86 (51)
C(7)–C(6)–C(5)	105.58 (36)	N–C(8)–C(9)	110.30 (38)
S(2)–C(2)–C(3)	115.26 (28)		

[a] Prime indicates the symmetry equivalent atom at (−*x*, *y*, $^1/_2$ − *z*).

Table VI. Planes for $Cu(S_4N_2C_{17}H_{24})^a$

plane	*a*	*b*	*c*	*d*
CuSS′	0.2431	0	0.9700	3.071
CuNN′	0.9194	0	0.3933	0.3058

[a] Planes are in orthonormal (Å) coordinates, defined by $aZ + bY + cZ = d$.

also be detected by noting the small difference between the formal C(2)–S(1) double bond length in the chelate ring of 1.7225 (38) Å and the C(2)–S(2) single bond length outside the chelate ring of 1.7716 (38) Å. In addition, an "extra" strain exists in the C(3)–C(4) bond resulting from the five-membered cyclopentene ring, and this may play a role in this bond length being slightly longer than expected.

Since we know the structure of this CuN_2S_2 chromophore, it is worthwhile to consider testing the sort of ligand field calculations which have been applied as a structural aid to both the type I copper(II) protein centers and the inorganic complexes in the past.[37,38] Using the technique described by Companion,[39] we determined the energies of the ligand field bands in this compound. The two sets of input parameters and resulting energies are shown in Table VII. Even though the calculation assumes only a d-orbital basis set, the results are remarkable. We determine that all four d–d bands should occur around 11 cm^{-1} × 10^3, and we note that only one very broad asymmetrical band is observed in the optical spectrum of this compound. Gray has used this approach successfully previously both to calculate expected bond angles and to predict positions of new d–d bands in type I copper(II) proteins.[37] This system represents a good check of such an approach.

Table VII. Input Parameters and Calculated Transition Energies from Crystal Field Calculation of CuN_2S_2 Chromophore^a

Input Parameters

atom	θ, deg	ϕ, deg	α_4	α_2/α_4
N	45.56	52.8	−10	1
N′	45.65	232.8	−10	1
S	133.34	0	(−8)(−7)^b	1
S′	133.34	180	(−8)(−7)	1

Resultant Transition Energies^c

transition^d	case I^e	case II^f
$^2B \rightarrow {}^2B(2)$	11.4	10.9
$^2B \rightarrow {}^2A(1)$	11.8	11.2
$^2B \rightarrow {}^2A(2)$	11.9	11.3
$^2B \rightarrow {}^2A(3)$	13.1	12.5

[a] See ref 39 for definition of input parameters. [b] Two cases for α_4 were considered for the sulfur atoms. [c] Energy values in cm^{-1} × 10^3. [d] In the pure rotational group C_2, $d_{x^2-y^2}$, d_{xy}, and d_{z^2} transform with A symmetry and d_{yz} and d_{xz} transform with B symmetry. The ^2B ground state and ^2B excited state, in the coordinate system chosen here (*z* as principal axis, CuS_2 in *xz* plane), are a linear combination of the d_{yz} and d_{xz} orbitals. The first and second ^2A excited states contain contributions from $d_{x^2-y^2}$, d_{xy}, and d_{z^2} orbitals. The third ^2A excited state is *primarily* $d_{x^2-y^2}$ and d_{xy} in character. [e] $\alpha_4(S) = -8$. [f] $\alpha_4(S) = -7$.

Among the three type I copper(II) centers represented by stellacyanin, plastocyanin, and azurin, only azurin has a band in this region (10.3 cm^{-1} × 10^3) which is ascribed to "d–d" in origin.[3-8] Manipulation of the input parameters of this ligand field calculation indicates that lower "d–d" bands occur with higher twist angles and weaker ligand fields. If we assume that only sulfur and nitrogen coordinations occur at these centers, then a higher twist angle is the only alternative to affect the spectrum.

It is also worthwhile pointing out that the plots of either $A_{\parallel}$ vs. $g_{\parallel}$ or $A_{\parallel}$ vs. the position of the highest d–d band in a series of copper(II) N_2S_2 complexes are essentially linear.[25,26,40] An extension of either of these plots intersects data for several copper(II) type I proteins as was suggested by Yokoi and Addison.[41] This observation is only significant in that it suggests that the thioketone sulfur ligand atom may be adequate for modeling the spectral role of sulfur in the copper(II) sites. We are in the process of considering several new CuN_2S_2 complexes where higher twist angles may result from steric factors, and those results will be available in the near future to test this hypothesis.

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Registry No. $Cu(S_4N_2C_{17}H_{24})$, 70814-01-6.

Supplementary Material Available: A listing of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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