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Structural Implications for Blue Protein Copper Centers from Electron Spin Resonance Spectra of Cu^{II}S_4 Chromophores¹

Sir:

Current interest in copper(II)-sulfur bonding has been stimulated by the finding of the copper(II)-sulfur (cysteine) bond being involved in the copper centers in "blue" copper proteins.² It has recently been shown³⁻⁵ that the intense blue coloration and high positive redox potentials in these proteins can be mimicked by simple inorganic compounds containing copper(II)-sulfur bonding. However, the origin of the anomalously small hyperfine (hf) coupling constants in the electron spin resonance (ESR) spectra of "blue" proteins is as yet uncertain.^{6,7} Several compounds containing copper(II)-sulfur bond(s) have been proposed as models for the "blue" copper centers, but they all show too large $|A_{||}|$ and/or $g_{||}$ values.⁸⁻¹⁰ Thus, the proposed spatial disposition of ligand atoms around the "blue" copper centers varies from flattened tetrahedral,¹¹ trigonal-bipyramidal,¹² and pentacoordinated¹³ to planar.^{3,4} The diversity of these models appears to result mainly from the paucity of pertinent ESR data, especially for tetrahedral copper(II) centers containing copper(II)-sulfur bonding.

We wish to report here preliminary results from single-crystal ESR measurements for a tetrahedral Cu^{II}S_4 center, in comparison with the ESR data for an appropriate square planar Cu^{II}S_4 center in a frozen glass. The tetrahedral Cu^{II}S_4 centers were produced by ⁶⁰Co γ -irradiation of a single crystal of tetrakis(thioacetamide)copper(I) chloride, a technique originally used for generation of copper(II) sites in a copper(I) lattice in the case of $\text{Cu}(\text{CH}_3\text{CN})_4^{2+}$.⁹ All experiments were performed at liquid nitrogen temperature. The generation of two copper(II) species was observed; the angular variation of the g values of the dominant species is depicted in Figure 1. If an irradiated crystal was allowed to warm to near-ambient temperature, the resonances attributable to cupric centers disappeared, as has been observed previously for a tetrahedrally distorted Cu^{II}S_4 species.¹⁰

Our preliminary result shows that (i) the ESR spectra of the major Cu^{II}S_4 center produced by γ -irradiation can be described by $g_x = g_y = 2.027$, $g_z = 2.152$, $|A_x| = |A_y| = 24$, $|A_z| = 86.9 \times 10^{-4} \text{ cm}^{-1}$, (ii) the principal axes of the g and A tensors coincide with each other, and (iii) the z axis is parallel to the crystallographic c axis. In this tetragonal crystal the copper(I) ion is surrounded almost tetrahedrally by four sulfur atoms in S_4 symmetry, and the dihedral angle between CuS_2 planes is 84.2° .¹⁴ The crystal c axis is the direction of compression (flattening) of the CuS_4 tetrahedra. Since (i) the lowest field lines show splitting characteristic of the isotopes ⁶³Cu and ⁶⁵Cu, (ii) no ligand superhyperfine structure was observed, (iii) the principal g and A values are both small, which is expected for sulfur coordination,⁷ (iv) the symmetry of the g and A tensors is as high as the crystal symmetry, and (v) the $g_{||}$, $|A_{||}|$ data lie in the $|A_{||}|$, $g_{||}$ region defined by the

Table I. Comparison of ESR Data of Copper Compounds Containing CuS_4 or Tetrahedral Coordination

Compd ^a	Core	Geom-etry ^b	$g_{ }$	$ A_{ } $ (10^{-4} cm^{-1})	Ref
$[\text{Cu}(\text{S}=\text{C}(\text{CH}_3)\text{-NH}_2)_4]^{2+}$	CuS_4	t	2.152	86.9	c
Cu^{2+} in tmtd	CuS_4	t?	2.1253	91.9	d
$\text{Cu}(\text{SPh}_2\text{PNPPh}_2\text{S})_2$	CuS_4	?	2.107	119	e
$(\text{Cu}:\text{Zn})(\text{S}_2\text{CNEt}_2)_2$	CuS_4	p	2.107	143	f
$[\text{Cu}(\text{TTP})]^{2+}$	CuS_4	p	2.086	147	c
$[\text{Cu}:\text{Ni}(\text{TTP})]\text{BF}_4$	CuS_4	p	2.087	172	g
$(\text{Cu}:\text{Ni})(\text{S}_2\text{P}(\text{OEt})_2)_2$	CuS_4	p	2.0855	150.6	h
$[(\text{Cu}:\text{Ni})(i\text{-mnt})_2]^{2-}$	CuS_4	p	2.086	156.0	h
$(\text{Cu}:\text{Ni})(\text{S}_2\text{CNEt}_2)_2$	CuS_4	p	2.0856	156.2	h
$[(\text{Cu}:\text{Ni})(\text{mnt})_2]^{2-}$	CuS_4	p	2.0837	160.5	h
$[(\text{Cu}:\text{Ni})(\text{S}_2\text{C}_2\text{O}_2)_2]^{2-}$	CuS_4	p	2.0805	163.9	h
$[\text{Cu}(\text{FDT})_2]^{2-}$	CuS_4	p?	2.094	177.1	i
$[\text{Cu}(\text{NCCH}_3)_4]^{2+}$	CuN_4	t?	~ 2.32	~ 80	j
$[\text{Cu}(\text{NCS})_4]^{2-}$	CuN_4	t	~ 2.43	89	k

^a Abbreviations: tmtd, tetramethylthiourea disulfide; i-mnt, 1,1-dicyano-2,2-dithioethylene; FDT, fulvenedithiolate; TTP, 1,4,8,11-tetrathiacyclotetradecane. ^b t, tetrahedral; p, planar. ^c This work: the minor component has $|A_{||}| = 69.4 \times 10^{-4} \text{ cm}^{-1}$, $g_{||} = 2.080$. ^d Reference 19. ^e Reference 10. ^f M. J. Weeks and J. P. Fackler, *Inorg. Chem.*, **7**, 2548 (1968). ^g L. K. White and R. L. Belford, *J. Am. Chem. Soc.*, **98**, 4428 (1976). ^h B. Malmström, B. Reinhammer, and T. Vännngård, *Biochim. Biophys. Acta*, **156**, 67 (1968); **205**, 48 (1970). J. Peisach, W. G. Levine, and W. E. Blumberg, *J. Biol. Chem.*, **242**, 2847 (1967). ⁱ P. C. Savino and R. D. Bereman, *Inorg. Chem.*, **12**, 173 (1973). ^j Reference 9. ^k K. D. Forster and V. Weiss, *J. Phys. Chem.*, **72**, 2669 (1968).

other CuS_4 centers (vide infra), these paramagnetic centers are certainly due to tetrahedral Cu^{II}S_4 chromophores.

Both perchlorate and tetrafluoroborate salts of the planar macrocycle^{3,4} $\text{Cu}(\text{TTP})^{2+}$ gave essentially the same ESR spectrum, characterized by small $g_{||}$ and moderately large $|A_{||}|$ values, in line with other planar Cu^{II}S_4 moieties (TTP, 1,4,8,11-tetrathiacyclotetradecane).

Table I summarizes all the available ESR data for Cu^{II}S_4 and tetrahedrally coordinated copper(II) centers, with biologically reasonable donor atoms. An examination of Table I, coupled with the data for planar or distorted octahedral compounds,¹⁵ reveals the following salient features: (i) all of the Cu^{II}S_4 centers show small $g_{||}$ values, ~ 2.09 to ~ 2.15 , (ii) the (flattened) tetrahedral coordination produces small $|A_{||}|$ values, which are half or less than half of those for planar or distorted octahedral centers,¹⁵ (iii) as for CuN_4 centers,¹⁶ the $g_{||}$ values of the CuS_4 loci decrease as $|A_{||}|$ increases (Figure 2, a schema of the $|A_{||}|$ vs. $g_{||}$ values for CuS_4 and CuN_4 centers, reiterates the correlation^{7,10,16} between these parameters for a given set of donor atoms and shows an almost linear relationship between them).

Peisach and Blumberg⁷ have shown that positive charge on a five-atom CuX_4 core can reduce $|A_{||}|$ and increase $g_{||}$. The effect is greater for CuS_4 than for CuN_4 centers,⁷ but is less influential for nitrogen-bonded copper than is the now well-established effect of tetrahedral distortion on planar CuN_4 moieties,¹⁶ which is also to decrease $|A_{||}|$ and increase $g_{||}$.

The ESR results for $\text{Cu}(\text{TTP})^{2+}$ suggest that the charge factor alone cannot reduce $|A_{||}|$ to the level observed for blue protein copper. Comparison of our data with that of Davis et al.,¹⁷ for $\text{Cu}(\text{TTP})^{2+}$ in the Ni-complex lattice as a planar CuS_4 unit with one weakly interacting BF_4^- , shows in addition that the effect of axial (ligand) perturbation of the CuS_4 square is to reduce $|A_{||}|$ by only 15%, as expected.¹⁸ We therefore propose that the above data enable a choice to be made in favor

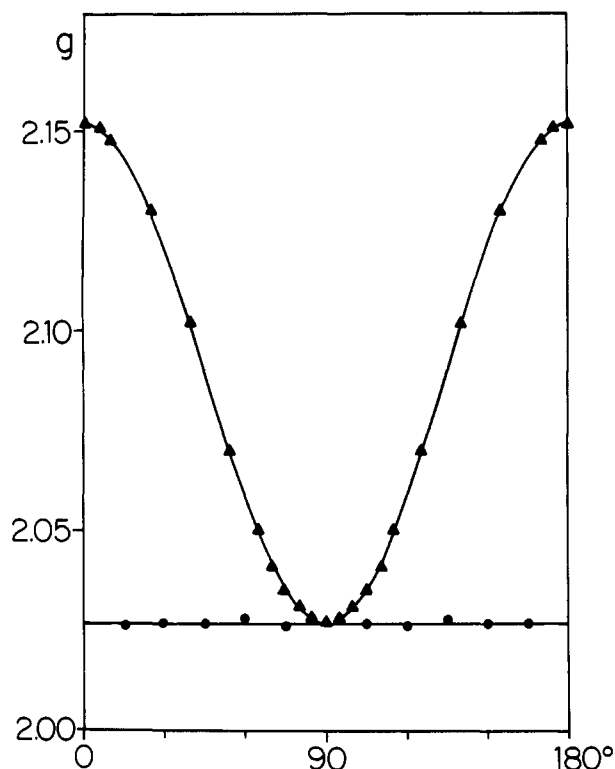


Figure 1. Angular variation of g values for the major copper(II) site in a γ -irradiated $\text{Cu}(\text{thioacetamide})\text{Cl}$ single crystal at 77 K. Rotation about the crystal c axis (perpendicular to the applied field) denoted by the points ●, rotation about the axis perpendicular to the (± 110) faces by the points ▲.

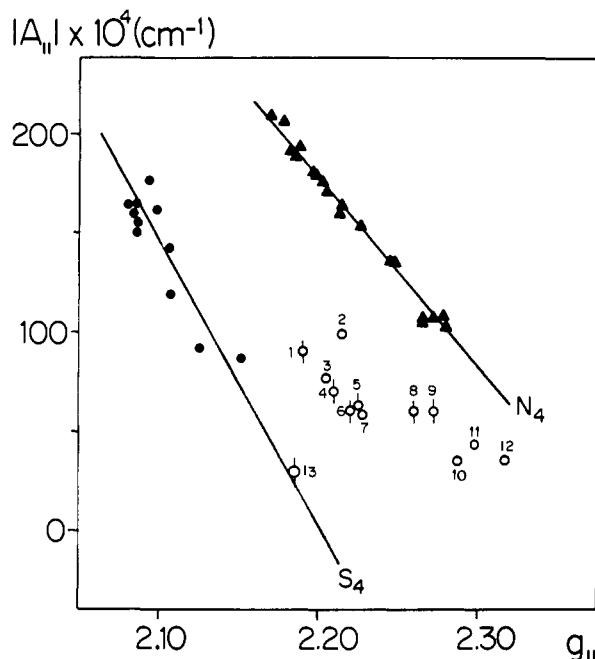


Figure 2. Schema of $g_{||}$ vs. $|A_{||}|$ for CuS_4 , CuN_4 , and blue protein copper centers. The CuN_4 line is based on data for pyrrole-2-aldiminate and dipyrromethenate copper(II) chelates.¹⁶ The open circles are data taken from ref 6a for blue copper proteins: 1, *P. versicolor* laccase; 2, 3, human ceruloplasmin components; 4, *R. succedanea* laccase; 5, spinach plastocyanin; 6, *C. sativus*, and 7, zucchini ascorbate oxidases; 8, *P. aeruginosa* azurin; 9, *B. pertussis* azurin; 10, *R. vernicifera* stellacyanin, and 11, laccase; 12, horseradish umecyanin; 13, cytochrome-*c* oxidase (from data given by F. T. Greenaway, G. Vincow, and S. H. P. Chan, the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 29–Sept 3, 1976).

of a tetrahedral copper geometry in blue copper proteins, as opposed to a square-planar geometry. Further, Figure 1

suggests that the ESR parameters of blue copper centers are compatible with CuS_2N_2 or CuSN_3 coordination, although the low value of $|A_{||}|$ found in such systems is not accounted for by a charge, tetrahedral distortion, or environmental effect alone. The lower symmetry associated with an N_2S_2 or N_3S donor atom set may contribute.

We note that Figure 2 corroborates the assignment of pseudotetrahedral CuS_4 coordination in Cu^{2+} -doped tetramethylthiourea disulfide.¹⁹

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Direct Stacking and Metal-Metal Interactions in Dithioacetato Palladium(II) Complexes

Sir:

Multinuclear d^8 - d^{10} metal ion complexes with sulfur-containing ligands are receiving considerable interest.¹ The wide variety of metal-metal interactions and of structural types which is being found in this class of compounds has important implications to topics such as the localized bonding description of the M-M interactions, the nature of the factors influencing M-M bond formation, the consequences of the M-M bond on the overall stereochemistry and electronic structure of the molecules etc.

Our present understanding of the M-M bonding in compounds of this type has been summarized by Fackler¹ recently. Previous work in the field from these laboratories has centered on nickel(II) dithiocarboxylates.^{2,3}

We have now obtained the dithioacetato derivatives of