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- (7) Hydrocarbon products were analyzed by analytical vapor phase chromatography (VPC) (Carbowax 400, 25 °C) and compared with authentic samples. Absolute yields were determined using *n*-octane as an internal standard.
- (8) The purple solution is introduced via Teflon tubing connected to sample injection ports into a specially designed copper-jacketed quartz cell attached to a cryogenic system<sup>9</sup> maintained at -78 °C.
- (9) Air Products Laboratory cryogenic system, Model LC-1-100 liquid nitrogen Dewar assembly, Model WMX-1A optical shroud with injector ports.
- (10) A rough estimate of the extinction coefficient ( $\epsilon$ ) can be made based on the hydrocarbon yield. We calculate  $\epsilon \sim 13$ , for the  $n \rightarrow \pi^*$  electronic transition of the 1,1-diazene.
- (11) Nils Wiberg and coworkers<sup>12</sup> recently reported the pyrolysis of lithium tosylhydrazide which deposited on surfaces cooled by liquid nitrogen a lustrous yellow solid diazene—*trans*-1,2-diazene (diimide)—which had  $\lambda_{\max}$  386 nm. The pyrolysis of cesium tosylhydrazide deposits a different diazene which had  $\lambda_{\max}$  260 nm. Wiberg was not able to assign this "other" diazene isomer to the *cis*-1,2-diazene or 1,1-diazene.
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- (15) Part of the blue shift could arise from the destabilization of the Franck-Condon excited state in the hydrogen bonding solvent.<sup>16</sup>
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- (17) The N=N stretching vibration of a symmetrical *trans* azo compound is forbidden in the infrared but absorbs in the 1576-cm<sup>-1</sup> (6.35  $\mu$ ) region of the Raman spectrum.<sup>16</sup>
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### A Structural Model for Type 3 Copper in Multicopper Oxidases

Sir:

In the multicopper (blue) oxidases type 3 copper exists in an EPR-nondetectable form and is associated with a two-electron accepting unit.<sup>1</sup> Magnetic susceptibility studies on oxidized *Rhus vernicifera* laccase (*p*-diphenol:O<sub>2</sub> oxidoreductase, E.C. 1.10.3.2) have established that the two type 3 copper atoms are present as an antiferromagnetically coupled Cu(II) dimer.<sup>2</sup> Although ligands bridging the coppers have not been positively identified, and other structural information is scanty, models incorporating two mercaptides or a disulfide as bridging ligands have received the most attention.<sup>1,3</sup> In conjunction with our investigation of mercaptide-bridged intramolecular electron transfer,<sup>4</sup> we have prepared and deter-

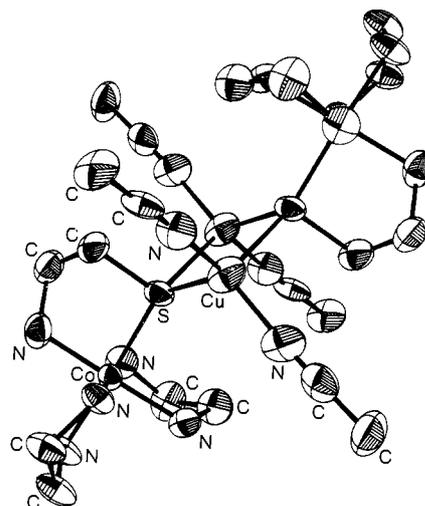


Figure 1. ORTEP drawing of the  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)\cdot\text{Cu}(\text{CH}_3\text{CN})_2]_2^{6+}$  cation. The 50% thermal probability ellipsoids are shown for all nonhydrogen atoms. Unlabeled atoms are related to the labeled ones by the crystallographic center of inversion.

mined by x-ray diffraction methods the crystal and molecular structure of  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)\cdot\text{Cu}(\text{CH}_3\text{CN})_2]_2\cdot(\text{ClO}_4)_6\cdot 2\text{H}_2\text{O}$  (en = ethylenediamine) which contains a unique  $\text{Cu}(\text{I})_2(\text{SR})_2$  planar unit. We believe this to be the first report of definitive structural information for such a copper-sulfur structure which is directly related to proposed models for the reduced form of type 3 copper in multicopper oxidases.

Addition of a concentrated solution of  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]_2^{2+}$  (perchlorate salt) in 0.1 M  $\text{HClO}_4$  to excess solid  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{ClO}_4$ , followed by filtration, precipitation with solid sodium perchlorate, and recrystallization from dilute  $\text{HClO}_4$ - $\text{NaClO}_4$  (all operations carried out under a nitrogen atmosphere), yields dull red-brown crystals which, when dry, are stable to air for several weeks. In an anaerobic 0.1 M  $\text{HClO}_4$ , a solution prepared from the crystals exhibits an absorption ( $\lambda_{\max}$  365 nm ( $\epsilon$  2900)) indistinguishable from that observed for the 1:1 complex formed between  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)]_2^{2+}$  and aqueous  $\text{Cu}(\text{I})^+$  in which coordination of copper to sulfur is required by the fact that sulfur is the only potential ligand bridge between the two metals and is further supported by the disappearance of the sulfur-to-cobalt charge-transfer transition from 282 nm in the starting complex<sup>5</sup> and the appearance of a new band at 365 nm upon incorporation of  $\text{Cu}(\text{I})$ .

The adduct formed rectangular crystals which were monoclinic, space group  $P2_1/c$ , with two molecules in a cell of dimensions  $a = 10.070$  (3) Å,  $b = 24.447$  (5) Å,  $c = 11.497$  (3) Å,  $\beta = 110.32$  (4)°. The calculated density was 1.795 g/cm<sup>3</sup> for  $Z = 2$ , which compared well with the measured density of 1.74 (5) determined by flotation in ethylene bromide-chloroform. The intensity data were collected on an Enraf-Nonius CAD-4 diffractometer using the  $\omega$ - $2\theta$  scan technique and  $\text{Mo K}\alpha$  radiation. The structure was solved by direct methods using MULTAN; nonhydrogen atomic parameters were refined by full-matrix least-squares calculations using the 2246 independent observed reflections. The  $R$  value after anisotropic refinement of all nonhydrogen atoms was 0.096. Two of the three symmetry-distinct perchlorate groups were disordered and will be treated in the final refinement of the structure.

The structure consists of two cobalt(III)-mercaptide-copper(I) moieties linked by mercaptide bridges between the copper atoms as shown in Figure 1. The crystallographic inversion center is located within the resulting  $\text{Cu}_2(\text{SR})_2$  planar

**Table I.** Selected Distances and Angles for the  $\text{Cu}_2(\text{SR})_2$  Core of  $[\text{Co}(\text{en})_2(\text{SCH}_2\text{CH}_2\text{NH}_2)\cdot\text{Cu}(\text{CH}_3\text{CN})_2]_2(\text{ClO}_4)_6\cdot 2\text{H}_2\text{O}$ 

Type	Distance, Å	Type	Angle, deg
Cu-S	2.406 (4) <sup>a</sup> 2.342 (5)	S-Cu-S	97.0 (1)
Cu-N	1.951 (1) 1.951 (2)	N-Cu-N	118.3 (5)
Cu-Cu	3.146 (2)	N-Cu-S	117.1 (5) 105.4 (5)
S-S	3.557 (6)	Cu-S-Cu	83.0 (1)
S-Co	2.273 (5)	Cu-S-Co	137.2 (2) 127.7 (2)
S-C	1.84 (2)	Cu-S-C	102.8 (5) 105.2 (5)
Cu-Co	4.356 (3) 4.142 (3)	Co-S-C	96.9 (6)

<sup>a</sup> Estimated standard deviations are in parentheses.

unit. Pertinent bond lengths and angles are presented in Table I.

Each copper is bound to two mercaptide sulfurs and two acetonitrile nitrogens in a distorted tetrahedral configuration. The copper-copper distance, although too great for consideration of substantial metal-metal bonding, is not out of line with that expected for a reduced type 3 copper site in view of the predicted *maximum* separation of 5–6 Å for antiferromagnetically coupled coppers in oxidized type 3 copper sites.<sup>1b</sup> The S-Cu-S bond angle (97°) indicates that the planar ring imparts, or at least allows, a geometry about the copper atoms intermediate between that preferred by copper(I) (tetrahedral) and copper(II) (tetragonal), a fact which may be of importance in the oxidation-reduction behavior of type 3 copper.

A disulfide bond can be ruled out on the basis of the sulfur-sulfur distance. Of note, however, is the fact that each sulfur is simultaneously bound to the two coppers, one  $sp^3$  carbon and one cobalt. It is thus conceivable that in the multicopper oxidases a cysteine sulfur atom, in addition to its function as a bridge between the two metals of the type 3 copper unit, serves as a further ligand bridge and as a mediator of intramolecular electron transfer between type 3 and type 1 or 2 copper chromophores. The possibility of such a structural arrangement in proteins, either in the ground state or in an electron-transfer transition state, seems worthy of serious consideration in view of the known facile inner-sphere electron-transfer mediating ability of coordinated mercaptide<sup>5,6</sup> and the kinetics of reduction of *Rhus vernicifera* laccase wherein reduction by hydroquinone indicated intramolecular electron transfer from type 2 to type 3 copper<sup>7</sup> and reduction by ferrocyanide suggested a common rate-determining step for reduction of type 1 and type 3 copper sites.<sup>8</sup>

Irradiation of the Co(III)-S-Cu(I) species (anaerobic, acidic solution) at 366 nm results in a decrease in intensity of the 365-nm absorption of the complex with concomitant production of aqueous Co(II) which suggests that the 365-nm absorption is due to either a primarily S → Co(III) or Cu(I) → S charge-transfer transition. The 365-nm band may thus result from a red shift of the S → Co(III) transition upon incorporation of Cu(I) into the complex. Alternatively coordination of Cu(I) to sulfur may give rise to a Cu(I) → S charge transfer centered at 365 nm while the S → Co(III) transition is shifted further into the ultraviolet where it is lost under other intense bands. From the available data we are unable to definitively choose between these alternatives. However, incorporation of  $\text{CH}_3\text{Hg}^+$  into the starting cobalt complex results in a blue shift of the S → Co(III) charge-transfer band of ~10 nm while Ag(I) yields a red shift of <5 nm.<sup>9</sup> Since there is no a priori reason to expect Cu(I) binding to result in a red shift

of the S → Co(III) transition of over 80 nm, and since Cu(I) → ligand transitions in the vicinity of 360 nm have previously been observed,<sup>10</sup> we prefer the second possibility.

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## References and Notes

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## Gas Phase Basicity of Silanamines

Sir:

There is abundant evidence for the dichotomous donor-acceptor behavior of a trimethylsilyl (TMS) group.<sup>1</sup> For example, the relative basicities of the amines  $\text{Me}_3\text{MCH}_2\text{NH}_2^2$  and acidities of the carboxylic acids  $\text{Me}_3\text{MCH}_2\text{CO}_2\text{H}^3$  (M = C, Si) indicate that a trimethylsilyl group releases electrons more strongly than a *tert*-butyl group (Table I); the reported  $\delta$  values for  $\text{Me}_3\text{SiCH}_2^-$  range from -0.1 to -0.2.<sup>4</sup> This behavior is commensurate with the relative electronegativities and polarizabilities of carbon and silicon.<sup>5</sup> The trend is reversed, however, upon direct attachment of a trimethylsilyl group to a  $\pi$ -electron system. Under many, but not all, circumstances, the TMS group behaves as a weak electron acceptor. Examples of this phenomena are numerous and can be found in qualitative studies of basicity of silanamines and ethers,<sup>6</sup> linear free-energy relationships,<sup>7</sup> and spectroscopic investigations of unsaturated organosilicon derivatives.<sup>8</sup> The most frequently cited explanation for this observation involves  $d\pi-\pi$  bonding,<sup>9</sup> although the necessity of including d orbitals in the bonding description has been questioned.<sup>10</sup>

The importance of determining intrinsic, solvent-free, substituent effects in simple acid-base chemistry is well recognized.<sup>11</sup> In this communication we describe the results of our efforts to obtain a quantitative measure of the proton affinities of a number of silanamines and their carbon analogues. Our

**Table I.** Aqueous  $pK_A$  Values for  $\text{Me}_3\text{MCH}_2\text{X}$  (25 °C)

M	X	
	$\text{NH}_2^a$	$\text{CO}_2\text{H}^b$
C	11.0	5.0
Si	10.2	5.22

<sup>a</sup> Reference 2. <sup>b</sup> Reference 3.