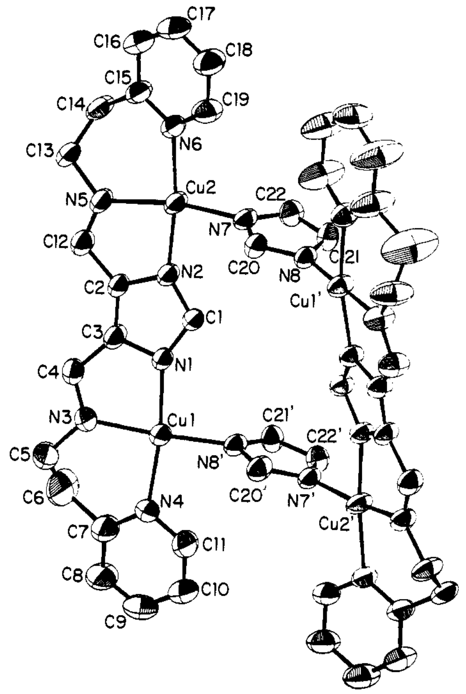

Figure 1. Structure of $[Cu_2(bpim)(im)]_2^{4+}$ showing the 40% probability thermal ellipsoids. Axially coordinated water and nitrate ligands and hydrogen atoms are omitted from the drawing. Selected bond distances (in Å, esd ~0.01 Å) are: Cu1-N1, 2.008; Cu1-N3, 1.992; Cu1-N4, 2.097; Cu1-N8′, 1.972; Cu2-N2, 1.992; Cu2-N5, 2.009; Cu2-N6, 2.056; Cu2-N7, 1.964; Cu1···Cu2, 6.214; Cu1···Cu2′, 5.910. Selected bond angles (in degrees, esd ~0.3°) are: N1-Cu1-N3, 81.6; N3-Cu1-N4, 89.1; N4-Cu1-N8′, 94.2; N8′-Cu1-N1, 94.7; N2-Cu2-N5, 80.8; N5-Cu2-N6, 91.3; N6-Cu2-N7, 98.3; N7-Cu2-N2, 89.7. Copper atoms are all within ±0.3 Å of the planes defined by the bridging imidazolate rings. A crystallographically required twofold axis relates the primed and unprimed atoms. The best planes through the two $Cu_2(bpim)$ halves of the dimer intersect with a dihedral angle of 136.5°.

The compounds containing II and III are soluble in polar solvents such as methanol or water. The ease with which II is converted into III upon addition of imidazole is striking. This process was investigated in more detail by carrying out pH titrations of a 2 mM aqueous solution of $[Cu_2(bpim)(im)]_2(NO_3)_4 \cdot 4H_2O$ at 25°, ionic strength 0.16. This complex reversibly takes up four protons between the end points at pH 9.75 and 4.25. The midpoint occurs at pH ~7 where there might be a slight inflection. Spectroscopic studies in water show the copper d → d band to shift from 608 nm at pH 10 to 649 nm at pH 4. The pH titration data are therefore tentatively interpreted according to eq 1. The possibility that reversible, pH dependent imidazolate-bridge-splitting reactions such as eq 1 might occur at the active site of bovine SOD has been discussed previously.[11]

$$\mathrm{III} + 4H^+ \rightleftharpoons 2\mathrm{II} + 2\mathrm{imH_2}^+ \qquad (1)$$

Magnetic susceptibility studies of III by the Faraday method on solid samples over the temperature range $4.5\ K < T < 320\ K$ show the copper centers to be antiferromagnetically coupled. A maximum occurs at 160 K in the susceptibility vs. T plot and the compound is diamagnetic below 35 K. Since the four copper(II) centers are connected by two different kinds of imidazolate bridges, analysis of the spin exchange (currently in progress) will require at least two coupling constants (J) in the Hamiltonian. It may be noted that a value of ~52 cm^{-1} was estimated for $-2J$ from the temperature dependence of the EPR spectrum in an active derivative of bovine SOD in which copper(II) had been substituted into the zinc(II) site of the enzyme.[12]

Acknowledgments. This work was supported by NIH research Grant No. GM-16449 from the National Institute of General Medical Sciences and by Grant No. MPS75-05243 from the National Science Foundation. We thank Dr. E. Breslow of Cornell University Medical College for advice about the potentiometric titrations, Dr. A. P. Ginsberg of The Bell Laboratories for providing magnetic data below 80 K, and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant applied to the purchase of the computer-controlled diffractometer.

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(10) Calcd for $C_{44}H_{52}N_{20}O_{16}Cu_4$: C, 38.54; H, 3.82; N, 20.43. Found: C, 38.37; H, 3.72; N, 20.53. If one water molecule is removed from the formula, the calculated percentages are: C, 39.06; H, 3.72; N, 20.70, and the density becomes 1.652 g/cm^3, in better agreement with the experimental value. The x-ray structure analysis reveals that one lattice water is disordered and perhaps should be given only partial occupancy. This point is being pursued further.

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Received May 24, 1976

The Crystal and Molecular Structures of $[(C_6H_5)_4P]_2Fe(S_2C_4O_2)_2$ and $[(C_6H_5)_4P]_2Fe(SC_6H_5)_4$, a Structural Analogue of Reduced Rubredoxin

Sir:

A variety of non-heme, iron-sulfur, proteins have been examined by spectroscopic and x-ray crystallographic studies. These, redox active, metalloproteins have been grouped into three general types, and the proposed or determined structures for the iron-containing sites form the basis of this classification.[1] In these sites the iron atoms are coordinated by deprotonated cysteinyl sulfur atoms (S-Cys), inorganic sulfide ions (S*), or both of these ligands. The basic iron-sulfur cores, present in each of these major types are: (a) $Fe(S\text{-}Cys)_4$, in rubredoxins (Rd); (b) $Fe_2S^*_2(S\text{-}Cys)_4$, in bacterial, plant, and mammalian ferredoxins (Fd); and (c) $Fe_4S^*_4(S\text{-}Cys)_4$, in "high-potential" (HP), and certain 4- and 8-Fe bacterial ferredoxins.

The tetrahedral 1-Fe site has been established by x-ray crystallography in Rd_{ox} from Clostridium pasteurianum.[2] The 4-Fe "cubane" structure has been determined for the active site in HP_{red} from Chromatium,[3] and for the two, nearly identical, $Fe_4S^*_4(S\text{-}Cys)_4$ clusters in the 8-Fe, Fd_{ox} from Peptococcus aerogenes.[4] Synthetic analogues of all three structural types of these active sites have been obtained and structurally characterized by Holm, Ibers, and co-workers. These investigators have characterized in detail successful electronic analogues for the active sites of HP_{red}, 4- and 8-Fe

Table I. Crystal and Refinement Data

	(I) $[(C_6H_5)_4P]_2$ $Fe(S_2C_4O_2)_2$	(III) $[(C_6H_5)_4P]_2$ $Fe(SC_6H_5)_4$
Cell dimensions (Å, deg)	a = 17.402 (7) b = 16.680 (5) c = 18.242 (6) β = 110.53 (2)	a = 13.797 (3) b = 17.542 (4) c = 24.913 (5)
Space group	$P2_{1/c}$, $Z = 4$	$Pbc2_1$, $Z = 4$
d_{calcd} (g/cm^3)	1.374	1.290
d_{obsd}[a]	1 .38 (1)	1.29 (1)
Crystal dimensions (mm)	0.1 × 0.3 × 0.2	0.1 × 0.3 × 0.2
μ, cm^{-1}	2.99	4.88
2θ(max)(deg)	40	30
Unique reflections	4624	1435
Reflections used $F^2 > 3\sigma(F^2)$	2801	999
Parameters	308	208
R_1[b]	0.057	0.042
R_2[c]	0.070	0.055

[a] Determined by flotation in CCl_4/pentane. [b] $R_1 = \Sigma|\Delta F|/\Sigma|F_0|$. [c] $R_2 = [\Sigma w(\Delta F)^2/\Sigma w|F_0|^2]^{1/2}$.

Table II. Selected Structural Parameters (Å, deg) in the $Fe(S_2C_4O_2)_2^{2-}$ and $Fe(SC_6H_5)_4^{2-}$ Anions

	(I) $Fe(S_2C_4O_2)_2^{2-}$	(III) $Fe(SC_6H_5)_4^{2-}$ [b]
M-S_1	2.380 (3)	2.353 (6)
M-S_2	2.394 (3)	2.372 (6)
M-S_3	2.397 (3)	2.338 (6)
M-S_4	2.387 (3)	2.359 (6)
S_1-S_2 (bite)	3.535 (5)	3.555 (10)
S_3-S_4 (bite)	3.551 (5)	3.630 (10)
S_1-S_3 (other)	4.234 (5)	4.052 (10)
S_2-S_4 (other)	4.015 (5)	3.985 (10)
S_1-Fe-S_2	95.53 (11)	97.58 (30)
S_3-Fe-S_4	95.84 (12)	101.21 (27)
S_1-Fe-S_3	124.84 (13)	119.47 (32)
S_2-Fe-S_4	114.23 (12)	114.76 (29)
S_1-Fe-S_4	115.11 (13)	113.36 (31)
S_2-Fe-S_3	112.47 (12)	111.23 (32)
Fe-S-C[a]	92.1 (8)	111.1 (1.5)
Dihedral Angles		
(S_1-Fe-S_3); (S_2-Fe-S_4)	78.26	81.58
(S_1-Fe-S_4); (S_2-Fe-S_3)	105.58	102.01
(S_1-Fe-S_2); (S_3-Fe-S_4)	94.19	93.68

[a] Average value, $\sigma = [\sum_{i=1}^{N}(\chi_i - \overline{\chi})^2/(N-1)]^{1/2}$ where χ_i is the size of the angle and $\overline{\chi}$ is the mean value for the N equivalent bond angles. [b] The apparently large standard deviations in this structure are the result of a limited number of, mostly high angle, reflections. At present a new data set (5286 unique reflections) has been obtained on a larger crystal and is being refined, following an absorption correction.

Fd_{ox}, 2-Fe Fd_{ox}, and 1-Fe Rd_{ox} proteins.[5] To date, the structure of an analogue of the Rd_{red} active site, which involves Fe(II)-mercaptide, tetrahedral coordination, has not been reported.[6] The only mononuclear Fe(II)-S_4 tetrahedral complexes previously prepared are the $Fe[(SPMe_2)_2N]_2$ and $Fe(Boc\text{-}Gly(Cys\text{-}Gly\text{-}Cys)_3\text{-}Cys\text{-}Gly\text{-}NH_2]^{2-}$. Of these, the former[7] does not contain the iron-mercaptide (RS^-) type of coordination, while the latter[8] was generated in solution but not isolated.

Recently, we reported[9] on the synthesis and characterization of three Fe(II) sulfur tetrahedral complexes, the bis(dithiosquarate)iron(II), $Fe(Dts)_2^{2-}$ (I), the dithiosquaratebis(thiophenolato)iron(II), $[Fe(Dts)(SPh)_2]^{2-}$ (II), and the tetrakis(thiophenolato)iron(II), $Fe(SPh)_4^{2-}$ (III). The Mössbauer spectra of these complexes were reported.[10] The isomer shifts, quadrupole splittings, and spectra in an applied field were compared to corresponding parameters in Rd_{red}.[11] All three of the complexes showed similar isomer shifts; however, only III showed a quadrupole splitting nearly unaffected by changes in temperature from 295 to 4.2 K. This temperature behavior, the magnitude of the quadrupole splitting, and the structural features of the spectra recorded in an applied field, for III, were nearly identical with those reported for Rd_{red}.[11] These similarities suggest that III has comparable hyperfine interaction and a fine structure term of similar symmetry and magnitude as reduced rubredoxin. It should be noted that the spin Hamiltonian parameters used to simulate the low temperature, high field spectra of Rd_{red} from Clostridium Pasteurianum,[12] also can be used[13] for the nearly exact simulation of the spectra of III. In this communication we report the crystal and molecular structures of I and III.

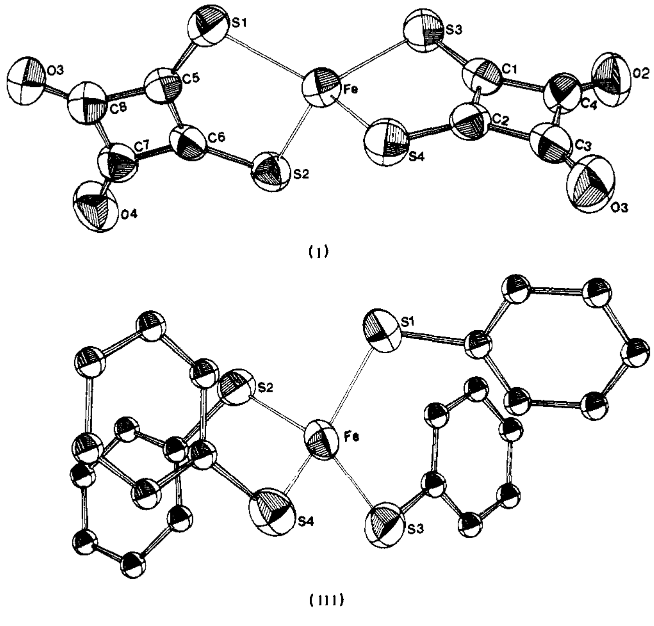

Figure 1. Structures and labeling of the FeS_4 cores of the $Fe(Dts)_2^{2-}$ (I) and $Fe(SPh)_4^{2-}$ (III) complexes. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965) represent the 50% probability surfaces.

Crystal and refinement data for the two structures are shown in Table I. Intensity data were obtained on a Picker FACS I automatic diffractometer using a step-scan technique employing graphite monochromatized Mo Kα radiation (λ 0.7107 Å, $2\theta_m$ = 12.2°). The structures were solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares calculations (Table I). All phenyl groups in the two structures were treated as rigid bodies[14] with the hydrogen atoms attached and the individual carbon temperature factors refined (C-C = 1.390 Å, C-H = 0.95 Å). Nongroup atoms were refined anisotropically. Structural details for the two complex anions are presented in Table II. See paragraph at end of paper regarding supplementary material.

The Fe(II) ions in both structures are four coordinate. The FeS_4 units are distorted tetrahedra and the distortions present in the two structures are remarkably similar. To a first approximation these distortions can be envisioned as a compression of each of the tetrahedra along one of their twofold axes. On closer examination, the compression appears to affect two of the sulfur atoms to a greater extent than the other two. This significant difference, present in both structures, is clearly evident in the S_1-Fe-S_3 angle compared to the S_2-Fe-S_4 angle and the S_1-S_3 and S_2-S_4 distances, respectively (Table II, Figure 1). The relatively short S_1-S_2 and S_3-S_4 distances are very similar in both structures and suggest that in the case of the $Fe(Dts)_2{}^{2-}$ complex ligand-"bite" constraints probably are not responsible for the observed distortion of the FeS_4 unit. It should be noted that the observed intraligand S-S distances in the coordinated Dts ligands (Table II) are *shorter* than the one expected for the free ligand.[15] Since it seems highly unlikely that the same crystal packing forces are present in both lattices, the very similar distortions found in both structures most probably are due to inherent electronic characteristics of the Fe(II) ions,[16] and quite likely are a manifestation of a pseudo-Jahn-Teller effect expected for tetrahedral iron(II). The average Fe-S bond length (2.389 Å) in I is significantly longer than the average Fe-S bond length (2.355 Å) in III. Both of these values are similar to the one reported[7] for $Fe[(SPMe_2)_2N]_2$, but are appreciably longer than the Fe(III)-S bond length in the $Fe(S_2\text{-}o\text{-xylyl})_2{}^-$ anion[5b] or the Fe-S_4 core in Rd_{ox}.[2] The structural parameters of the two independent dithiosquarate ligands in I are similar to those reported for the $Ni(Dts)_2{}^{2-}$ complex.[9a]

It is apparent that the observed differences in the Mössbauer spectra[10] between I and III cannot be accounted for solely on the basis of deviations from tetrahedral symmetry. Electron delocalization properties of the ligands and charge density at the sulfur donors must be important. The longer Fe-S bond lengths in I compared to III may indicate differences in these properties for the dithiosquarate and thiophenolate ligands, respectively.

Acknowledgments. The financial support of this project by a grant (1R01 GM 18144-01A1) from the U.S. Public Health Service is gratefully acknowledged. The authors also are thankful to Dr. C. Murphy for growing the single crystals which were used for the collection of data.

Supplementary Material Available: Observed structure factors (24 pages). Ordering information is available on any current masthead page.

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(16) To establish this point we are presently undertaking a crystal structure determination of the x-ray isomorphous Co(II) complex.
(17) Alfred P. Sloan Fellow, 1972-1974.

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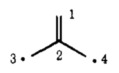
Received May 27, 1976

The Influence of Substituents on the Molecular Orbital Energies and Ground Electronic States of Substituted Trimethylenemethanes[1]

Sir:

In the simple Hückel approximation, π-electron molecular orbital (MO) theory predicts a degenerate pair of nonbonding energy levels (ψ_2 and ψ_3) for D_{3h} unsubstituted trimethylenemethane, **1**,[2] in accord with the experimental observation[3] of a triplet ground state. However, although unsymmetrical substitution or geometric distortion from threefold symmetry can lift the simple Hückel orbital degeneracy, membership in a highly symmetrical molecular point group is neither in principle[4] nor in fact a necessary condition for a triplet ground state, as the case of the diyl **2d** demonstrates.[5]



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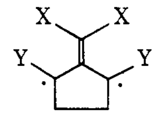

2a, X = OMe; Y = H
b, X = acceptor; Y = donor
c, X = donor; Y = acceptor
d, X = CH_3; Y = H

Recent more elaborate quantum mechanical calculations[6-12] suggest that the lowest singlet state of **1** may lie as much as 18-21 kcal/mol above the triplet. If this is correct, one might expect ground state triplet character to survive rather severe perturbations of the parent trimethylenemethane (TMM) structure. We report here qualitative arguments and semiempirical quantitative calculations that provide a theoretical basis for the discussion of substituent effects on the ordering of spin states and on the chemical behavior of TMM derivatives. Other papers[13,14] contain experimental tests of some of the conclusions.

The degeneracy of ψ_2 and ψ_3 persists even in C_{2v} TMM at the simple Hückel (HMO) level. At a higher level of approximation, contraction of one C-C-C angle lifts the degeneracy because of the resulting nonnearest neighbor interaction.[9b] However, it can be shown by a zero differential overlap (ZDO) calculation[8,15] that the effect remains too small to reverse the singlet-triplet ordering, even for unique angles as small as 90°. Moreover, a graph theoretical procedure[16] now shows that substitution of any combination of alternant hydrocarbon residues (e.g., phenyl, vinyl, etc.) is without effect on the HMO orbital degeneracy, even when such substitution removes all