tion in the case of ^{23}Na(I) in aqueous solution gives $R_1 \simeq 10^{-2}$ sec^{-1}. In ^{205}Tl solutions the experimental relaxation rate is much faster than this, but if the larger size of this ion is taken into account, an even smaller relaxation rate would be expected.

The accelerated relaxation rate of ^{205}Tl(I) in a pure aqueous solution is similar to an effect that has been reported for ^{129}Xe in liquid xenon.[14] The explanation in the case of ^{129}Xe is a fluctuating local magnetic field associated with rotating distorted spherical orbitals during Xe/Xe collisions. This has been called a "transient spin-rotation relaxation."[15] If Tl(I)/Tl(I) encounters in solution are very frequent and also give a random local magnetic field, it is possible that this mechanism contributes to relaxation of ^{205}Tl(I) in aqueous solution. A scalar interaction of the "first kind," discussed by Abragam,[16] between ^{205}Tl(I) and ^{203}Tl(I) is another possible mechanism. This unusual relaxation pathway for aqueous solutions would render the relaxation rates of ^{205}Tl(I) and ^{203}Tl(I) equal. Measurements of the relaxation rates of ^{203}Tl(I) (spin $^1/_2$, 30% abundant) give values equal to those for ^{205}Tl(I) reported in Table I within experimental error.

In all relaxation mechanisms, R_1 is dependent on rotational and translational correlation times in the liquid which can be empirically treated in terms of the macroscopic viscosity. An interesting feature of the tabulated values of R_1 is that the ratios for $R_1(D_2O)/R_1(H_2O)$ are the same as the ratios of the macroscopic viscosities of pure D_2O and H_2O at 25°. This infers that the relaxation mechanism is the same in H_2O and D_2O.

The results reported here point out the need for scrupulous care in purifying materials and preparing samples to avoid molecular oxygen and other paramagnetic impurities. Work is proceeding to determine the nature of the oxygen complex using both nmr and other techniques.

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A Novel Compound with a Planar Fe–S–S–Fe Bridge and Its Possible Relation to Ferredoxins[1]

Sir:

In exploring iron–sulfur chemistry which may have a bearing on structure and function in the ferredoxin class of proteins,[2] we have synthesized a compound, [CpFe(SC$_2$H$_5$)S]$_2$ (Cp = cyclopentadienyl), whose X-ray crystal structure, shown in Figure 1, reveals a novel feature: a planar Fe–S–S–Fe bridge (see Table I). The

(2) J. C. M. Tsibris and R. W. Woody, *Coord. Chem. Rev.*, 5, 417 (1970).
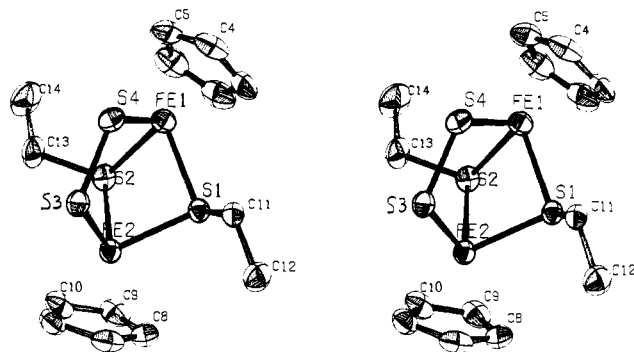

Figure 1. ORTEP stereodrawing of [CpFe(SC$_2$H$_5$)S]$_2$ showing the anisotropic thermal ellipsoids.

Table I. Least-Squares Plane of the Fe–S–S–Fe Bridge

| Atom	$0.6879X + 0.5451Y - 0.4793Z = 7.7909$ Dev, Å	Atom	Dev, Å
Fe(1)	+0.003	S(3)	+0.012
Fe(2)	−0.003	S(4)	−0.014

ethyl sulfide ligands also bridge the two iron atoms, while the π-cyclopentadienyl groups complete the roughly octahedral iron coordination spheres. The iron–iron separation, 3.31 Å, is nonbonding.[3] Other distances and angles, given in Table II, are unexcep-

Table II. Interatomic Distances (Å) and Angles (deg)[a]

Distances			
Fe(1)–Fe(2)	3.307 (3)	Fe(2)–S(2)	2.285 (5)
Fe(1)–S(1)	2.273 (5)	Fe(2)–S(3)	2.129 (5)
Fe(1)–S(4)	2.129 (5)	Fe(2)–S(1)	2.275 (5)
Fe(1)–S(2)	2.289 (5)	S(3)–S(4)	2.023 (7)
Angles			
S(1)–Fe(1)–S(2)	76.44 (5)	S(1)–Fe(2)–S(2)	76.50 (5)
S(1)–Fe(1)–S(4)	94.31 (5)	S(1)–Fe(2)–S(3)	93.98 (5)
S(2)–Fe(1)–S(4)	93.43 (5)	S(2)–Fe(2)–S(3)	94.17 (5)
Fe(1)–S(1)–Fe(2)	93.28 (5)	Fe(1)–S(4)–S(3)	107.76 (6)
Fe(1)–S(2)–Fe(2)	92.62 (5)	Fe(2)–S(3)–S(4)	107.33 (6)

[a] Standard deviations in parentheses refer to the least significant digit.

tional. While a M–S–S–M bridge is unprecedented, there are several analogous *peroxide* and *superoxide* bridges in binuclear cobalt(III) complexes,[4] e.g.

$$(NH_3)_4Co \overset{O—O}{\underset{NH_2}{\diagdown\diagup}} Co(NH_3)_4{}^{4+}$$
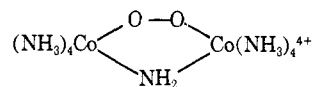
Moreover, a similar structure involving Fe(III) atoms has been suggested for the oxy form of the oxygen binding protein hemerythrin.[5,6]

The nmr spectrum of [CpFe(SC$_2$H$_5$)S]$_2$ shows a *sharp* cyclopentadienyl resonance at τ 5.27 (compare τ 5.68 for diamagnetic [Cp(CO)Fe(SCH$_3$)]$_2$[7]). Susceptibility measurements on a Gouy balance confirm that the

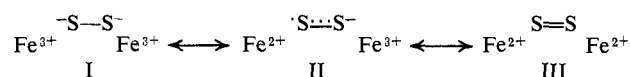(3) N. G. Connelly and L. F. Dahl, *J. Amer. Chem. Soc.*, 92, 7472 (1970).
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compound is essentially diamagnetic at room temperature. While the cyclopentadienyl ligands probably force the iron atoms into a low-spin configuration, the absence of appreciable paramagnetism is still surprising since allocation of charge in the conventional manner, i.e., Cp^-, $C_2H_5S^-$, and S_2^{2-}, leaves Fe^{3+} ions, with at least one unpaired electron each, there being no metal–metal bond. If, on the other hand, the iron atoms are spin-paired Fe^{2+}, then the two sulfur atoms must be formulated as S_2^0. There are, in fact, three plausible resonance forms

$$\underset{\substack{Fe^{3+} \qquad Fe^{3+} \\ I}}{^-S-S^-} \longleftrightarrow \underset{\substack{Fe^{2+} \qquad Fe^{3+} \\ II}}{\cdot S \dot{\cdots} S^-} \longleftrightarrow \underset{\substack{Fe^{2+} \qquad Fe^{2+} \\ III}}{S=S}$$

and the structure suggests that form II predominates. The dihedral angle about the S–S bond is $0°$, as it is for the superoxide bridge in

$$(NH_3)_4Co \overset{O-O}{\underset{NH_2}{<\quad>}} Co(NH_3)_4{}^{4+}$$
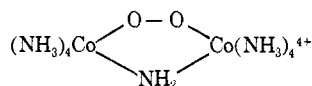
whereas a dihedral angle close to $90°$ is normal for disulfides.[8] Moreover, the S–S distance, 2.02 Å, is shorter than the expected single bond distance, 2.10 Å, for a planar cis disulfide and suggests a π bond order of about one-third.[8] The distance in double bonded $S_2^0({}^3\Sigma_g{}^-)$ is 1.889 Å.[9]

The apparent diamagnetism can also be ascribed to strong magnetic coupling between Fe^{3+} centers via the bridging ligands. Since a superexchange mechanism involves a degree of electron transfer from the bridging ligand to the coupled metal atoms,[10] this formulation is equivalent to electron delocalization through the above resonance forms. A modest contribution from resonance forms II and III would be sufficient to eliminate any observable paramagnetism at room temperature. Alternatively, superexchange might operate through the ethyl sulfide bridges.

The electronic structure of $[CpFe(SC_2H_5)S]_2$ should be capable of better definition through spectroscopic studies, which are currently underway. The redox chemistry is also of interest. A polarogram in acetonitrile (0.1 M $LiNO_3$) supporting electrolyte gave an anodic wave at 0.17 V vs. sce but no cathodic wave above the breakdown potential of the solvent. The dark green compound was obtained in low yield by alumina chromatography of the products of the reaction of $[CpFe(CO)_2]_2$ with ethyl polysulfide (a mixture of tri- and tetrasulfide) in refluxing methylcyclohexane.

The present work suggests an addition to the catalog of candidate structures[2] for those ferredoxins which contain two iron atoms and two labile sulfur atoms, viz.

$$cys-S-Fe \overset{S-S}{\underset{\underset{\underset{\underset{cys}{|}}{S}}{\underset{|}{S}}}{<\overset{cys}{|}>}} Fe-S-cys$$

A
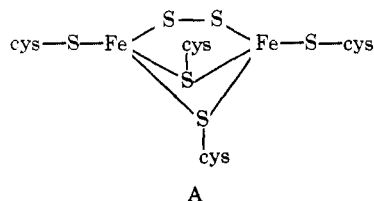
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(10) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968, p 193.

(cys = cysteine) structure A. Although it is now well established[11] that the reduced form of these proteins contains high-spin Fe(II) in a tetrahedral sulfur environment, strongly exchanged coupled to a high-spin Fe(III) partner, the oxidation state of the labile sulfur is still uncertain, both sulfide[12] and disulfide[13] being candidates. The possibility that cysteine sulfur is involved in bridging the iron atoms, as in structure A, is of interest in connection with the suggestion of Dunham, et al.,[11] that an apparent inconsistency between magnetic susceptibility and nmr data on reduced spinach ferredoxin can be resolved by assuming that a cysteine residue is under the influence of both Fe(II) and Fe(III) centers.

Structure Determination. The structure was solved by direct methods, on intensity data collected to $2\theta = 105°$, using the $\theta-2\theta$ scan technique on a Picker four-circle diffractometer, with Ni-filtered Cu $K\alpha$ radiation. The intensities of 1711 reflections were above 2σ. The data were corrected for Lorentz and polarization effects and for absorption. The transmission coefficient ranged from 0.157 to 0.257, based on a value of $\mu = 177.7$ cm^{-1}. Least-squares refinement, with anisotropic thermal parameters for all nonhydrogen atoms, gave a final R factor of 0.039. The crystal was monoclinic, space group $P2_1/c$, with four molecules of $[CpFe(SC_2H_5)S]_2$ per unit cell, of dimensions $a = 17.374$, $b = 8.125$, and $c = 12.782$ Å and $\beta = 108.37°$; $d_x = 1.661$, $d_m = 1.639$ g/cm^3 (flotation).

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Isopropylidenecyclobutenone

Sir:

The methylenecyclobutenone system represents one of the few remaining unknowns among the cyclobutadienes and related compounds.[1] Although several highly substituted derivatives are claimed,[2,3] they do not yield any information on the characteristics of the methylene-cyclobutenone moiety. We now report the synthesis of isopropylidenecyclobutenone (5), the first simple derivative in which the salient features of the ring system can be discerned.

Our synthesis route involved preparation of a suitable compound 2 which could yield 5 by Diels–Alder retrogression.[4] While this would not be expected to be successful for the synthesis of the unsubstituted cyclo-

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