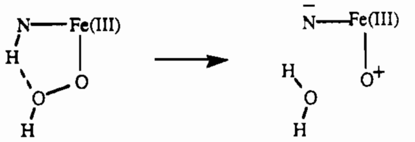
Since no parameters specific to Fe(III) are available,[16] parameters which are generally applicable to metal complexes were applied. The axial M–N bond lengths were set to be 0.1 Å longer than the equatorial ones, and the latter were varied from 1.9 to 2.1 Å. The bond stretching constants for the M–N bonds were set to be 0.4 mdyn/Å. Bending constants were set to 0.1 mdyn/rad for the anti N–M–N angles and were varied from 0.3 to 0.4 mdyn/rad for the remaining N–M–N angles. M–N bond dipoles were set to 0.8 D. The torsional parameters for all X–N–M–N dihedral angles were all set to zero.[17]

Four conformers with the NH_2 axial and two conformers with the imidazole axial were calculated.[18] The most stable structures are **4** and **5** (Figure 1) for the five- and six-coordinate complexes, respectively, both of which have the NH_2 axial. These structures match the X-ray structures reported by Mascharak quite well.[13,14,19] Structure **6** is another view of **4** rotated to show that the NH of the secondary amine is equatorial and is not suitable for hydrogen-bonding to a sixth ligand, O_2 or O_2H^-. Structure **7**, which has the imidazole axial, is calculated to be less stable than **6** by several kcal/mol, primarily due to out-of-plane coordination at the carboxamide N atom. Nevertheless, the NH bond of the secondary amine is axial and is in an ideal position to form hydrogen-bonding with a sixth O_2 or O_2H^- ligand. Therefore, this structure could become more stable with the addition of strong intramolecular hydrogen-bonding to a sixth ligand. Even if **7** does not become the more stable conformer when peroxide is bound, it may nevertheless be required for activation of the bound HOO^- ligand if internal hydrogen-bonding is required to facilitate OH^- loss (eq 1). It has been shown that intramolecular hydrogen-bonding often plays an important role in activating oxygen atom transfer reactions.[20-23] Such hydrogen-bonding is especially important for heterolytic O–O bond cleavage, since negative charge develops on the leaving O.



(1)

This hydrogen-bonding model can also nicely rationalize some puzzling observations reported by Ohno and co-workers concerning the relative yields of epoxidation of *cis*- and *trans*-stilbenes by another Fe–BLM model, Fe–PYML, using H_2O_2 as the oxidant.[7] They found that the reaction of *trans*-stilbene is significantly suppressed by *tert*-butyl groups attached to their PYML ligand. If one assumes either that O–O bond cleavage precedes the reaction with olefin and that the reactive species is a high-valent iron oxo or that O–O bond cleavage is concerted with the reaction with olefin but the peroxide ligand is not pinned down by hydrogen-bonding, it is difficult to understand why *tert*-butyl groups on the ligand would interfere with the reaction with *trans*-stilbene but not *cis*-stilbene (see **9** in Figure 2).[24] On the other hand, in the case where the peroxide ligand is hydrogen-bonded to the PYML ligand and where epoxidation is concerted with O–O bond cleavage,[25] the formation of the hydrogen bond restricts the direction of alkene attack.[26] The attack of *cis*-stilbene may occur readily in this structure, as in **8**, since the Ph groups can orient away from the *tert*-butyl group. However, the approach of *trans*-stilbene is unfavorable, because one of the Ph groups has to be positioned close to the *tert*-butyl group.[27]

Several qualitative conclusions can be derived from the current study: (1) without hydrogen-bonding, the favorable coordination of Fe–BLM is with the NH_2 axial; (2) activation of Fe–BLM by O_2 or H_2O_2 may involve a geometrical change to achieve internal hydrogen-bonding;[28,29] (3) the hydrogen-bonding model can rationalize the relative efficiency of epoxidation of *cis*- and *trans*-stilbenes by PYMLs and BLMs.

Acknowledgment. We are grateful to the National Institutes of Health (K.N.H.) and the National Science Foundation (J.S.V.) for financial support of this research. We thank Professors Pradip Mascharak and Jack Peisach for helpful discussions.

Registry No. BLM, 11056-06-7; Fe–BLM, 71801-37-1; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0.

Supplementary Material Available: Figure S1, showing calculated structures of five-coordinated metal complexes, and Tables S1 and S2, listing N–M–N bending angles in calculated structures and reported X-ray structures of metal–BLM complexes and the calculated relative energies of metal complexes (2 pages). Ordering information is given on any current masthead page.

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[18] The six structures and relative energies are given in Figure S1 and Table S2 of the supplementary material.

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[28] This geometrical change can be achieved easily. Since a five-coordinate intermediate exists in a square-pyramidal conformation, coordination of O_2 from different directions leads to different structures.

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Kinetics of Formation and Reactions of Thiyl Radicals in Aqueous Solution

Thiyl radicals are formed in biological systems when the sulfhydryl group acts as a radioprotector.[1-6] These radicals are of interest in electron-transfer reactions in inorganic[7-9] and

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Table I. Rate Constants (25 °C) for Hydrogen Abstraction by Carbon-Centered Radicals from Thiols (CysSH = Cysteine, GSH = Glutathione)[a]

$R'^{\bullet}$	RSH	pH	$k_2/10^7$ L mol^{-1} s^{-1}
$^{\bullet}CH_3$	CH_3SH	11	7.4[b]
	C_2H_5SH	1.0	4.0 ± 0.2
		7.0	4.7 ± 0.2
	CysSH	7.0	7.4 ± 0.2
	GSH	7.0	7.1 ± 0.2
$^{\bullet}CH_2CH_3$	C_2H_5SH	7.0	2.8 ± 0.1
$^{\bullet}CH_2OH$	$HOCH_2CH_2SH$	10	13[b]
	$NH_2CH_2CH_2SH$	7.6	6.8[c]
	$HSCH_2CH(OH)CH(OH)CH_2SH$	7	6.8[d]
	CysSH	7	4.2[e]
$^{\bullet}CH(OH)CH_3$	$HOCH_2CH_2SH$	10	23[c]
	$NH_2CH_2CH_2SH$	7.6	14[b]
$^{\bullet}CH_2CH_2OH$	$HOCH_2CH_2SH$	10	4.7[b]
$^{\bullet}C(CH_3)_2OH$	$HOCH_2CH_2SH$	10	51[b]

[a] Errors given are standard deviations in the data set as calculated by a nonlinear least-squares fitting program. [b] Reference 4. [c] Reference 2. [d] Reference 6. [e] Reference 1.

bioinorganic systems.[10-12] Also, sulfur-centered radicals are involved as intermediates in the oxidation of thiols.[13] The kinetic information that is available for reactions of thiyl radicals has largely been obtained by pulse radiolysis.[14-16] However, we have developed a simpler method for generating thiyl radicals and studying their reactions using laser flash photolysis. This method involves well-established reactions to generate thiyl radicals and allows the study of a wide variety of their reactions in aqueous solution. Since virtually nothing is known about the reactivity of thiyl radicals with metal complexes, we have applied this method to study their reactions with simple hexaaqua ions.

The method used in this study involved producing carbon-centered radicals (~1 × 10^{-6} M) by visible (490 nm) laser flash photolysis of aqueous solutions containing $RCo([14]aneN_4)(H_2O)^{2+}$ (eq 1).[17] With water-soluble ethanethiol, cysteine,

$$R'Co([14]aneN_4)^{2+} + h\nu \rightarrow R'^{\bullet} + Co([14]aneN_4)^{2+} \quad (1)$$

or glutathione present, the so-called "repair" reaction[1-6] was employed to generate thiyl radicals (eq 2). At high concentrations

$$R'^{\bullet} + RSH \rightarrow R'H + RS^{\bullet} \quad (2)$$

of thiol, virtually all the carbon-centered radicals react to form thiyl radicals. Thiyl radicals were allowed to react with $ABTS^{2-}$ in a known reaction (eq 3)[18-20] to yield $ABTS^{\bullet-}$ which was monitored at 650 nm (ϵ 1.2 × 10^4 L mol^{-1} cm^{-1}).[21]

$$RS^{\bullet} + ABTS^{2-} \rightarrow RS^{-} + ABTS^{\bullet-} \quad (3)$$

With $[ABTS^{2-}] \gg [RSH]$ (10^{-2} and 10^{-4} M, typically), reaction 2 is rate limiting. In keeping with that, the first-order rate constant is directly proportional to [RSH] and independent of $[ABTS^{2-}]$. Thus, the repair reaction can easily be studied for simple aliphatic carbon-centered radicals. Values of k_2 are listed in Table I along with selected literature values.

Table II. Rate Constants (25 °C) for Reactions of Thiyl Radicals with $ABTS^{2-}$ (2,2′-Azinobis(3-ethylbenzthiazoline-6-sulfonate) Ion)) and TMPD (*N,N,N′,N′*-Tetramethyl-*p*-phenylenediamine)[a]

probe	$RS^{\bullet}$	pH	$k_3/10^7$ L mol^{-1} s^{-1}
$ABTS^{2-}$	$C_2H_5S^{\bullet}$	1.0	5.6 ± 0.2
		7.0	50 ± 4
	$CysS^{\bullet}$	4.0	78 ± 2
		3.75	100[b]
		7.0	8.8 ± 0.2
TMPD	$C_2H_5S^{\bullet}$	7.0	260 ± 10

[a] Errors given are standard deviations in the data set as calculated by a nonlinear least-squares fitting program. [b] Reference 21.

When $[ABTS^{2-}] \ll [RSH]$, reaction 2 is rapid and rates of reaction of $RS^{\bullet}$ with $ABTS^{2-}$ can be determined. Under these conditions the rate constant is independent of [RSH] and directly proportional to $[ABTS^{2-}]$. The reaction of $RS^{\bullet}$ with TMPD[22] to form the highly colored $TMPD^{\bullet+}$ (ϵ_{565} 1.25 × 10^4 L mol^{-1} cm^{-1})[23] was also studied as an alternative spectroscopic probe. The results of the $ABTS^{2-}$ and TMPD studies are given in Table II. The rate constant for the reaction of $CysS^{\bullet}$ with $ABTS^{2-}$ at pH 7 has previously been reported[20] to be 5.0 × 10^8 L mol^{-1} s^{-1}, much larger than our value of 8.8 × 10^7 L mol^{-1} s^{-1}. However, the previous workers apparently had ascorbate present in their $ABTS^{2-}$ solutions, which may have increased the observed rate constants. Ascorbate is known to be oxidized by $CysS^{\bullet}$ with a rate constant of 1.2 × 10^9 L mol^{-1} s^{-1}.[24]

We have examined reactions between $C_2H_5S^{\bullet}$ and $M(H_2O)_6^{2+}$ (M = Cr, V, Fe). These experiments were also conducted with $ABTS^{2-}$ present. Rates were higher with $M(H_2O)_6^{2+}$ than without, since $C_2H_5S^{\bullet}$ branches between reactions 4a and 4b, with $ABTS^{\bullet-}$

$$RS^{\bullet} + M(H_2O)_6^{2+} \rightarrow (H_2O)_5MSR^{2+} + H_2O \quad (4a)$$

$$RS^{\bullet} + M(H_2O)_6^{2+} \rightarrow M(H_2O)_6^{3+} + RS^{-} \quad (4b)$$

buildup monitored as before. Values of k_4 measured at pH 1.0 at 25 °C are (4.9 ± 0.2) × 10^8 (Cr^{2+}), (6.5 ± 0.3) × 10^8 (V^{2+}), and (1.2 ± 0.1) × 10^6 L mol^{-1} s^{-1} (Fe^{2+}). At longer times, $ABTS^{\bullet-}$ is reduced (eq 5) by Cr^{2+} (k = 1.1 × 10^8) and V^{2+} (2.6 × 10^8 L mol^{-1} s^{-1}), but these reactions do not interfere.[25]

$$ABTS^{\bullet-} + M(H_2O)_6^{2+} \rightarrow ABTS^{2-} + M(H_2O)_6^{3+} \quad (5)$$

The reactions of thiyl radicals with Cr^{2+} occur about 2–5 times faster than those of alkyl radicals. The reaction with Cr^{2+} was expected to be an inner-sphere process (eq 4a) and to form stable (thiolato)chromium(III) as a product in analogy to reactions of $R^{\bullet}$, which form $(H_2O)_5CrR^{2+}$ complexes. Two similar compounds that are known to be stable for several hours are $(H_2O)_5CrSC_6H_4NH_3^{3+}$ and $(H_2O)_5CrSC_6H_4N(CH_3)_3^{3+}$.[26] Also known is the (hydrogensulfido)chromium(III) ion $(H_2O)_5CrSH^{2+}$.[27] Indeed, Cr^{2+} was observed to react with $C_2H_5S^{\bullet}$ by an inner-sphere mechanism. One of the bases for this claim consists of experiments in which the thiyl radical was formed by photolysis of diethyl disulfide. When the disulfide was photolyzed in the presence of Cr^{2+}, an increase in absorbance at wavelengths below 300 nm was observed, suggesting Cr–S bond formation. No free thiol was detected as a product gas chro-

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The kinetic results for Cr^{2+} were confirmed by an independent method without the use of $ABTS^{2-}$. Flash photolysis of EtSSEt at 266 nm with a Nd–YAG laser generated ethanethiyl radicals in the presence of Cr^{2+}. Product buildup at 280 nm, an absorption maximum for the (ethanethiolato)chromium(III) complex, gave $k_4 = 3.9 \times 10^8$ L mol^{-1} s^{-1}, in satisfactory agreement with the probe method.

The Fe^{2+} reaction with $C_2H_5S^{\bullet}$ is inferred to proceed by an inner-sphere mechanism, since its rate constant (1.2×10^6 L mol^{-1} s^{-1}) is comparable to that for the reaction of Br_2^- with Fe^{2+} (3.6×10^6 L mol^{-1} s^{-1}), which is known to be an inner-sphere process.[30] The relatively slow substitution rate for Fe^{3+} (ca. 10–10^2 L mol^{-1} s^{-1}) means it can be considered inert on the time scale of the oxidation by ethanethiyl radicals. However, the initial product of the reaction, presumably $(H_2O)_5FeSC_2H_5^{2+}$, was not observed, probably due to low extinction coefficients. Ethanethiol was detected as a final product gas chromatographically.

An outer-sphere mechanism for $V(H_2O)_6^{2+}$ is consistent with the slow ligand substitution of this ion. Attack of $RS^{\bullet}$ at a trigonal face may provide the site of electron transfer.[31,32] Ethanethiol was detected gas chromatographically.

The flash photolytic method described here may be applied to the study of the biologically significant cysteinyl and glutathionyl radicals without pulse radiolysis. It is particularly suited to the study of thiyl radicals with metal complexes and should prove useful in many inorganic and bioinorganic studies.

Acknowledgment. Support was provided by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, through Contract W-7405-Eng-82.

Registry No. $ABTS^{2-}$, 1180-72-9; TMPD, 100-22-1; $EtS^{\bullet}$, 14836-22-7; EtSSEt, 110-81-6; $Cr(H_2O)_6^{2+}$, 20574-26-9; $V(H_2O)_6^{2+}$, 15696-18-1; $Fe(H_2O)_6^{2+}$, 15365-81-8; $(H_2O)_5CrSC_2H_5^{2+}$, 138541-77-2; $MeCo([14]aneN_4)(H_2O)^{2+}$, 51240-12-1; $EtCo([14]aneN_4)(H_2O)^{2+}$, 111323-55-8; H_2, 1333-74-0; ethanethiol, 75-08-1; cysteine, 52-90-4; glutathione, 70-18-8; cysteine radical, 35772-84-0; glutathione radical, 40055-99-0.

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Synthesis and Structure of Mixed-Ligand Iron–Sulfur Cubane-like Clusters $[(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5]^n$ (n = 0 and 1+)

A number of transition metal clusters have been synthesized and structurally characterized[1,2] which possess M_4S_4 cubic cores with four supporting ligands on each metal. Most, however, carry the same supporting ligands on all metals, and clusters possessing different supporting ligands on a homometallic M_4S_4 core are rare.[3] Recently we reported the synthesis of the mixed-ligand iron-sulfur cubane cluster $(\eta\text{-}C_5Me_5)_2(Ph_2C_2S_2)_2Fe_4S_4$ (**1**) by the reaction of $(\eta\text{-}C_5Me_5)_2Fe_2(CO)_4$, S_8, and PhC≡CPh.[4,5] From the same reaction mixture, we have recently succeeded in the isolation of another mixed-ligand iron–sulfur cluster, $(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**), which was less stable than **1**. A cluster similar to **2** but carrying the same supporting ligands, $Cp_4Fe_4S_5$, has been reported by Kubas et al.[7] We now report the structural change which accompanies a one-electon oxidation of this cluster.

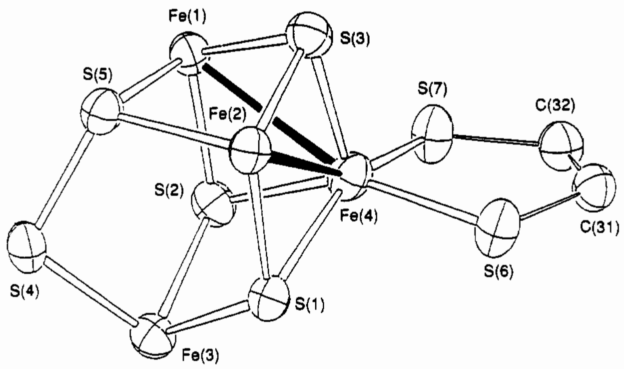
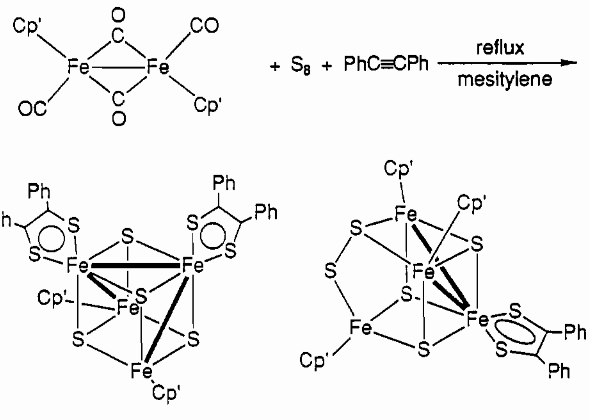


Figure 1. ORTEP drawing of the Fe_4S_5 core of $(\eta\text{-}C_5Me_5)_3(Ph_2C_2S_2)Fe_4S_5$ (**2**) with a dithiolene chelate ring. Thermal ellipsoids are plotted at the 50% probability level. Selected distances (Å): Fe(1)···Fe(2), 3.300 (1); Fe(1)···Fe(3), 3.769 (1); Fe(1)–Fe(4), 2.716 (1); Fe(2)···Fe(3), 3.760 (2); Fe(2)–Fe(4), 2.725 (1), Fe(3)···Fe(4), 3.307 (2).

The reaction between $(\eta\text{-}C_5Me_5)_2Fe_2(CO)_4$, S_8, and PhC≡CPh in a 1:0.5:1 ratio in refluxing mesitylene for 12 h[8] gave a brown reaction mixture containing **1** and **2** (eq 1). After removal of mesitylene in vacuo, the residue was chromatographed on silica gel which had been deactivated by prior treatment with acetone, since **2** was not stable on commercially available silica gel. By use of the deactivated silica gel, **2** was obtained as dark green crystals in 24% yield[9] together with **1** (41% yield). The single



(1)

1 **2**

Cp'=η-C5Me5

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