rotation, some bending motion must also be involved. There is also the possibility that use is made of the empty site beneath the basal plane. For Berry pseudorotation to occur, the required trigonal-bipyramidal intermediate would be severely distorted due to the small bite size of the 1,3-diene ligand.[13] However, fluxional behavior has been observed in the ^{13}C nmr spectrum of (butadiene)$Fe(CO)_3$.[24] Since nonconjugated 1,4- and 1,5-dienes, which span axial-equatorial sites of a trigonal bipyramid more easily, show a dramatic increase in fluxionality,[24] pseudorotation may be the mechanism involved in the rearrangement observed for these dieneiron carbonyl–trifluorophosphine systems.

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Registry No. (2,3-Dimethyl-1,3-butadiene)$Fe(PF_3)(CO)_2$, 52950-83-1; (*trans,trans*-2,4-hexadiene)$Fe(PF_3)(CO)_2$, 52950-82-0; (isoprene)$Fe(PF_3)(CO)_2$, 52950-80-8; (*trans*-1,3-pentadiene)$Fe(PF_3)(CO)_2$, 52950-81-9; (*cis*-1,3-pentadiene)$Fe(PF_3)(CO)_2$, 52993-18-7; (2,4-dimethyl-1,3-pentadiene)$Fe(PF_3)(CO)_2$, 52950-84-2; (1,3-butadiene)$Fe(PF_3)_3$, 52993-22-3; (2,3-dimethyl-1,3-butadiene)$Fe(PF_3)_3$, 52993-23-4; (*cis*-1,3-pentadiene)$Fe(PF_3)_3$, 52993-24-5; (*trans*-1,3-pentadiene)$Fe(PF_3)_3$, 52993-25-6; (2,4-dimethyl-1,3-pentadiene)$Fe(PF_3)_3$, 52993-26-7; (isoprene)$Fe(PF_3)_3$, 52993-27-8; (1,3-butadiene)$Fe(PF_3)_2(CO)$, 52993-20-1; (*trans,trans*-2,4-hexadiene)$Fe(PF_3)_2(CO)$, 52950-87-5; (2,3-dimethyl-1,3-butadiene)$Fe(PF_3)_2(CO)$, 52950-88-6; *trans*-(isoprene)$Fe(PF_3)_2(CO)$, 52993-21-2; *cis*-(isoprene)$Fe(PF_3)_2(CO)$, 52950-90-0; (*cis*-1,3-pentadiene)$Fe(PF_3)_2(CO)$, 52993-19-8; (*trans*-1,3-pentadiene)$Fe(PF_3)_2(CO)$, 52950-86-4; (2,4-dimethyl-1,3-pentadiene)$Fe(PF_3)_2(CO)$, 52950-89-7; 1,3-butadiene, 106-99-0; isoprene, 78-79-5; *trans*-1,3-pentadiene, 2004-70-8; 2-methyl-*trans*-1,3-pentadiene, 926-54-5; 4-methyl-1,3-pentadiene, 926-56-7; 2,4-dimethyl-1,3-pentadiene, 1000-86-8.

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Iron(II) and Cobalt(II) Complexes of Boc-(Gly-L-Cys-Gly)$_4$-NH_2 as Analogs for the Active Site of the Iron–Sulfur Protein Rubredoxin

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Iron(II) and cobalt(II) complexes of Boc-(Gly-L-Cys-Gly)$_4$-NH_2 have been synthesized in dimethyl sulfoxide. Evidence is presented that the iron complex is the first rubredoxin model incorporating a polypeptide backbone demonstrated to have a tetrahedral FeS_4 core.

Introduction

The iron–sulfur proteins[1] function in biological electron-transfer reactions.[2] The simplest class of these proteins is the rubredoxins[3] (red redox proteins). Rubredoxins isolated from anaerobes have mol wt *ca.* 6000. They contain a single iron atom but unlike other iron–sulfur proteins no *inorganic* sulfide. The polypeptide backbone has 50–60 amino acid residues, *four* of which are cysteines. Sequencing studies on a number of rubredoxins from anaerobes show that they all contain two well-separated -Cys-X-X-Cys- (X = amino acid) units.[4,5]

The X-ray structural studies by Jensen, *et al.*,[5] on the oxidized form of rubredoxin from *Clostridium pasteurianum* show that the iron atom is coordinated to only the *four* cysteinyl sulfurs with approximately tetrahedral geometry. A large number of physical studies have been performed on rubredoxins, in both oxidation states, which are generally in accord with their formulations as Fe^{II} and Fe^{III} complexes.[2,3]

Although its biological function is unknown, rubredoxin is, nevertheless, of interest to inorganic chemists for a variety of reasons: (i) the apoprotein is a tetradentate tetrathiolato ligand; (ii) it forms high-spin d^6 (Fe^{II}) and d^5 (Fe^{III}) complexes with an approximately tetrahedral FeS_4 core; in fact, oxidized rubredoxin is the only example of an iron(III) complex with this structural feature; (iii) rubredoxins are the only known compounds containing iron tetrahedrally coordinated to four sulfurs that undergo reversible iron(II)–iron(III) redox behavior[6] ($E_0' = -0.057$ V for *C. pasteurianum* rubredoxin[6]); (iv) the 1.5-Å X-ray data show that the Fe–S distance of

Cys-42 is 0.2–0.3 Å shorter than the others;[5] (v) the iron chromophore in the oxidized protein is remarkably stable and removal of the iron to give the apoprotein is relatively difficult;[7,8] (vi) the holoprotein can be reconstituted by the addition of the apoprotein and an excess of a sulfhydryl reagent (2-mercaptoethanol or dithiothreitol) at pH 10 to ferric or ferrous ion in the presence of oxygen.[7,8]

Attempts to prepare analogs with peptides and thiols have not previously yielded characterizable iron derivatives. The simple addition of L-cysteine to ferric ion gave complexes with S,O- or S,N-coordination.[9] The reaction of iron(III) with excess 2-mercaptoethanol and Na_2S at pH 9 gave an unstable species which was thought to have sulfide bridges and S,-O-coordinated 2-mercaptoethanol.[10] It was proposed that decomposition occured *via* iron(III)-catalyzed oxidation of thiol to disulfide. Similar observations have been reported for systems containing cysteine[11] or thioglycolate.[12] While our work was in progress, the decapeptides H-L-Cys-L-Thr-L-Leu-L-Cys-Gly-L-Cys-L-Pro-L-Leu-L-Cys-Gly-OH and the N-protected Boc derivative, corresponding to residues 6–10 and 38–42 of *Peptococcus aerogenes* rubredoxin, were added to solutions of 2-mercaptoethanol at pH 10, were treated with iron(II), and were exposed to air.[13] Although in each case a complex was formed, no information concerning the nature of the iron–sulfur centers was obtained.

We have synthesized[14] the dodecapeptide Boc-(Gly-L-Cys-Gly)-NH_2. Examination of molecular models showed that this peptide could easily form tetrahedral complexes. In this work we describe the reactions of this peptide with iron(II) and cobalt(II) species in the presence of tertiary amine bases in dimethyl sulfoxide. The resulting complexes are compared to iron(II) rubredoxin and simple coordination compounds with sulfur donors having a tetrahedral MS_4 core.

Experimental Section

General Data. The dodecapeptide Boc-(Gly-L-Cys-Gly)4-NH_2 was prepared as described previously.[14] The preparation of the complexes was carried out under an atmosphere of prepurified nitrogen and solution transfers were made in an efficient glove box. Solvents were carefully deoxygenated before use. The metal salts (Fe- and Co-$(DMSO)_6)(ClO_4)_2$ were prepared by literature methods.[15,16] Brucine was recrystallized from acetone–water and dried at 90° *in vacuo*. Triethylamine was distilled three times from naphthyl isocyanate prior to use. Electronic spectra were recorded on a Cary 17 spectrometer.

Preparations and Physical Studies. Preparations of the Iron(II) and Cobalt(II) Complexes of Boc-(Gly-L-Cys-Gly)4-NH_2. The hexakis(dimethyl sulfoxide)metal(II) perchlorates (1 equiv) and an equimolar amount of Boc-(Gly-L-Cys-Gly)4-NH_2 were dissolved in dimethyl sulfoxide. The spectra were simply those of $[M(DMSO)_6]^{2+}$ species. The addition of 4 equiv of a tertiary amine base (triethylamine or brucine) gave a colorless to very light violet solution for iron (λ_{max} 5100 cm^{-1}; ϵ 110 M^{-1} cm^{-1}, based on 100% complex formation) and a deep green solution for cobalt (λ_{max} (cm^{-1}) 6400 (sh), 7300 (sh), 7900, 13,000, 14,300, 16,700; ϵ (M^{-1} cm^{-1}), based upon 100% complex formation, 130, 166, 178, 376, 477, 320). These solutions were very air sensitive. The iron solution when exposed to air very rapidly became deep red-violet, which faded to orange in the course of 24 hr. For the cobalt solution exposure to air produced rapid decomposition to yield a yellow-brown solution. Electrochemical studies using a Princeton Applied Research Model 170 electrochemistry system on DMSO solutions *ca.* 10^{-3} *M* in complex and containing 0.1 *M* tetraethylammonium perchlorate supporting electrolyte gave irreproducible behavior and did not show any reversible or nearly rereversible one-electron oxidation waves.

Results and Discussion

The design of a peptide to serve as a minimal model for the protein backbone was governed by two features of the structure[5] of *C. pasteurianum* rubredoxin: (i) the cysteine residues occur in well-separated pairs, each with the sequence -Cys-X-X-Cys- where X is an amino acid; (ii) apart from its bonding contact with the four cysteinyl sulfur atoms, the iron

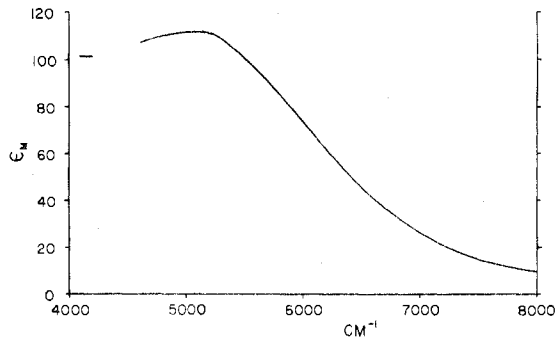


Figure 1. Near-infrared absorption spectrum of the brucinium salt of the iron(II)–peptide complex in dimethyl sulfoxide

atom apparently is not bonded to functional groups of other residues, including those in the loop between pairs of cysteine residues. Sequenced rubredoxins that have been isolated from the anaerobes *Peptostreptococcus elsdenii*[17] and *P. aerogenes*[18] and the aerobe *P. oleovarans*[19] all contain pairs of cysteine residues in the sequence -Cys-X-X-Cys-. The long loop which joins two such pairs in the backbone of rubredoxins has been reduced to two residues in this work, the minimum necessary to make the synthetic peptide a tetradentate chelate. To minimize the possibility of undesired competition the N terminus of the peptide was blocked through the use of the *tert*-butyloxycarbonyl (Boc) derivative, and the C terminus was the poorly coordinating amide function. The block synthesis of the dodecapeptide is described elsewhere.[14] The method of synthesis chosen was designed to introduce the L-Cys residue in an essentially racemization-free step and to provide versatility in the synthesis of other cysteinyl-containing oligopeptides[20] (*e.g.*, those having more residues in the loop, etc.). The metal salts $[Fe(DMSO)_6][ClO_4]_2$ and $[Co(DMSO)_6][ClO_4]_2$ and the tertiary bases (brucine and triethylamine) used to deprotonate the peptide tetrathiol were chosen to avoid the presence of strongly competing donor ligands in the nonaqueous chelation procedure. The properties of the complexes were independent of the base used.

Iron Complex. The iron(II) complex of Boc-(Gly-L-Cys-Gly)4-NH_2 was prepared as a colorless to violet solution that was very air sensitive. Upon air oxidation a deep red-violet color formed initially and became orange on prolonged standing. The near-infrared absorption spectrum of the iron(II) complex is shown in Figure 1 and contains a very broad band with a maximum at 5100 cm^{-1} (ϵ 110 M^{-1} cm^{-1}). The species is most probably monomeric; however, in the absence of definitive X-ray structural results, polymeric structures cannot be ruled out.

The broad band observed at 5100 cm^{-1} can be assigned with confidence to the $^5E \rightarrow {}^5T_2$ transition of high-spin tetrahedral iron(II) from comparison to species known to have tetrahedral Fe^{II}–S_4 coordination. Values of Δ_t of 3400, 2480, and 4470 cm^{-1} have been reported for tetrahedral iron(II) when doped into ZnS, CdTe, and $MgAl_2O_4$ lattices, respectively.[21] These species were postulated to have $^5T_2$ splittings of 535, 255, and 945 cm^{-1}, respectively, as a result of Jahn–Teller distortion of the tetrahedral symmetry. The complex $Fe(S_2PF_2)_2$ was considered to have tetrahedral stereochemistry, but no electronic spectrum was reported.[22] The magnetic moment of 5.2 BM is in the range 5.0–5.4 BM expected for tetrahedral high-spin iron(II); however, without further characterization the assignment must be viewed with caution.[23] The compound $[Fe(CH_3)_3AsS)_4](ClO_4)_2$ has a broad absorption at 5500 cm^{-1} and a magnetic moment consistent with high-spin tetrahedral iron(II).[24] Davison and Switkes[25] have reported the synthesis and characterization of $[(R_2PS)_2N]_2Fe$ (R = C_6H_5, CH_3). These species have solid- and solution-phase magnetic moments in the expected range and a ligand field transition centered

at *ca.* 3500 cm^{-1} (ϵ 120 M^{-1} cm^{-1}). Similarly, Davison and Reger[26] prepared $[((C_6H_5)_2PS)_2CH]_2Fe$, having solid- and solution-phase magnetic moments in the appropriate range and an electronic absorption centered at *ca.* 3800 cm^{-1} (ϵ 96 M^{-1} cm^{-1}). A single-crystal X-ray study of $[((CH_3)_2PS)_2N]_2Fe$ provided the first confirmation of a tetrahedral FeS_4 core in a simple iron(II) derivative.[27] The Fe–S distances range from 2.34 to 2.38 Å, whereas the distances in *oxidized* rubredoxin range from 2.05 to 2.34 Å. The S–Fe–S angles vary from 101 to 115°, a range similar to that found in rubredoxin.

Since initially reporting the observation of a d–d transition in reduced rubredoxin at 6250 cm^{-1} Eaton and Lovenberg have postulated the presence of three d–d bands in the near-infrared spectrum.[3] This postulate is based upon the premise of strong splitting of the $^5T_2$ state as a result of distortion from tetrahedral geometry. Although comparison of the X-ray data at 4-Å resolution for the reduced species with 4-Å data for oxidized rubredoxin indicates no apparent structural differences in the FeS_4 core, the detailed stereochemistry of reduced rubredoxin is not known with certainty. Indications that distortions are present in both the reduced and oxidized protein come from recent physical studies,[3,28,29] such as the large quadrupole splitting observed in the Mossbauer spectrum of reduced rubredoxin.[28] This result was interpreted to indicate a splitting of 850 cm^{-1} in the ^5E levels.[3] In the circular dichroism spectrum of reduced rubredoxin, bands at 6000 and 7400 cm^{-1} are present. A third band at *ca.* 3700 cm^{-1} was postulated based on features evident in the circular dichroism and absorption spectra in the range 4100–4700 cm^{-1} provided by a window in the D_2O solvent absorption. Thus the d orbitals were considered to be split into levels of relative energies 0, 850, 3700, 6000, and 7400 cm^{-1}, which involved a splitting of about 3000 cm^{-1} for the $^5T_2$ orbitals and a value of *ca.* 5000 cm^{-1} for Δ_t. In the crystal field model, such a pattern is consistent with lowering of tetrahedral symmetry to D_{2d} through tetragonal distortion or to C_{3v} through trigonal elongation of a Fe–S bond but not with the trigonal compression of that bond as found in the X-ray crystal structure of the oxidized protein.

The near-infrared spectrum provides compelling evidence that the iron(II)–peptide complex is the first model for rubredoxin that contains an iron atom tetrahedrally coordinated to four cysteine residues of a polypeptide chain. From the broad band with maximum at 5100 cm^{-1}, a value of Δ_t of about 4000–5000 cm^{-1} was estimated. Since the occurrence of strong vibrational bands prevented the continuation of the spectrum to lower energies, the full breadth of the absorption and possible presence of additional bands are uncertain. The visible spectrum of the complex has a weak band at 20,000 cm^{-1} superimposed upon a continuous-band spectrum that has strong absorptions at energies greater than 26,000 cm^{-1}. Upon exposure to air, the complex changes to a deep red-violet color, similar to the wine red color reported for oxidized rubredoxin. The band at 20,000 cm^{-1} intensifies rapidly, and its presence in the spectra of the iron(II) complex is attributed to traces of air or ferric ion in the salt $Fe(DMSO)_6(ClO_4)_2$. A weak shoulder at 17,000 cm^{-1} also becomes apparent. These features correspond closely to the bands at 20,200 cm^{-1} (495 nm) and 17,700 cm^{-1} (565 nm) reported for oxidized rubredoxin and provide strong evidence for the presence of a tetrahedral Fe^{III}–S_4 chromophore.

Attempts to isolate pure samples of the iron(II)–peptide complex are in progress; however, difficulties in the isolation may be anticipated to result from the presence of diastereomers I and and II. These species are diastereomers rather than enantiomers because of the chiral L-cysteine residues in the tetradentate ligand.

Although iron(III)–sulfur complexes are not uncommon,[30,31]

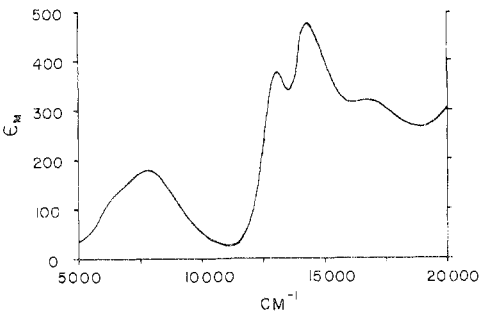
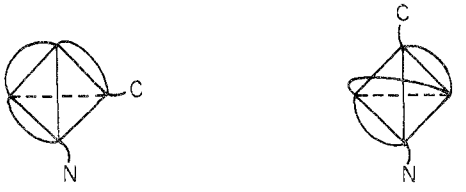
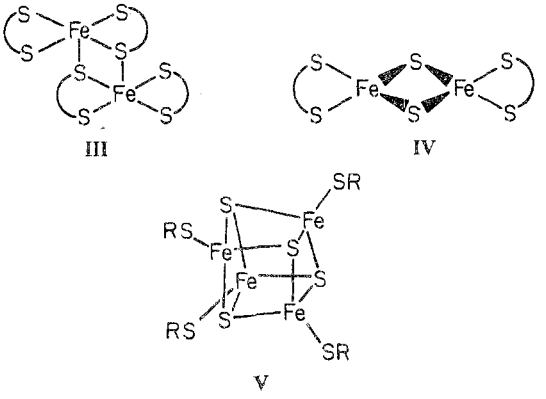


Figure 2. Absorption spectrum of the brucinium salt of the cobalt(II)–peptide complex in dimethyl sulfoxide



I II

rubredoxin is the single known compound with a tetrahedral Fe^{III}–S_4 core. Other compounds show a tendency to coordinate additional ligands. The iron atoms of the compound $[(C_4H_9)_4N]_2[Fe(SCH_2CH_2S)_2]_2$ (III) have approximately trigonal-bipyramidal stereochemistry as a result of bridging *via* the ethanethiol sulfur atoms.[31] A recent X-ray structural analysis of a model for the active center of 2Fe–2S* proteins[32] indicated that there are approximately tetrahedral Fe^{III}–S_4 centers (IV); however, the Fe–Fe distance is short enough for bonding interaction. Additional X-ray structural studies have shown that metal–metal bonding is also expected in the 4Fe–4S* clusters (V) found in iron–sulfur proteins[33,34] and associated model complexes.[35]



III IV

V

The study of the reversibility of this system is of importance. Initial polarographic results, however, do not indicate that the system is reversible.[36] Further work is necessary to elucidate the redox behavior of the iron–peptide complex both at electrode surfaces and in the presence of oxidizing and reducing agents.

Cobalt Complex. The cobalt complex of Boc-(Gly-L-Cys-Gly)$_4$-NH_2 was prepared as a green solution that oxidized readily upon exposure to the air to give a yellow-brown product. The electronic spectrum is shown in Figure 2 and has absorptions with energies and intensities typical of high-spin tetrahedral cobalt(II). This complex is considered to be monomeric; however, as in the case of the iron complex, definitive structural proof is lacking. Attempts to prepare pure samples of the solid are in progress, although, as noted previously for the iron(II) complex, the presence of diastereomers must be recognized.

The electronic spectrum of the cobalt(II)–peptide complex

Table I. Summary of Spectral Data for Cobalt Complexes

Complex	ν_2,[a] cm^{-1}	ν_3,[a] cm^{-1}	Δ_t, cm^{-1}	B', cm^{-1}	Ref
$[((CH_3)_2PS)_2N]_2Co$	6576	14,399	3831	632	25
$[((C_6H_5)_2PS)_2CH]_2Co$	6539	14,974	3804	674	26
$[Co(Boc\text{-}(Gly\text{-}L\text{-}Cys\text{-}Gly)_4\text{-}NH_2)]^{2-}$	7330	15,100	4295	636	This work

[a] Weighted averages of several maxima.

in dimethyl sulfoxide has bands corresponding to $\nu_2(^4A_2 \rightarrow {}^4T_1(F))$ centered at 7330 cm^{-1} and to $\nu_3(^4A_2 \rightarrow {}^4T_1(P))$ centered at 15,100 cm^{-1} of tetrahedral cobalt(II).[37] The color of the compound and the spectral features are very similar to those of the tetrahedral compounds $[(R_2PS)_2N]_2Co$ (R = C_6H_5, CH_3)[25] and $[((C_6H_5)_2PS)_2CH]_2Co$.[26] The data in Table I point out this similarity. The ligand field splitting Δ_t was calculated[38] to be 4295 cm^{-1}.

Conclusions

The electronic absorption spectra for the complexes of iron(II) and cobalt(II) with Boc-(Gly-L-Cys-Gly)4-NH2 provide strong evidence for the existence of the first rubredoxin analog that has tetrahedral coordination of iron to four cysteine residues of a polypeptide backbone. The values of Δ_t for the complexes are higher than for the simple inorganic analogs previously studied;[25,26] however, Δ_t for the iron complex is nevertheless lower than for reduced rubredoxin.[3] Such a difference indicates that although the iron(II)–peptide complex apparently provides a viable model to rubredoxin, the subtle differences brought about by the natural protein backbone may provide constraints that increase the ligand field.

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Registry No. Brucinium iron(II)–peptide complex, 53023-52-2; Brucinium cobalt(II)–peptide complex, 53023-53-3.

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