7   8

9   10

11, R = H   13
12, R = Ac

14   15

5.7 (4 H) m, and 4.6 (1 H) d (J = 9 Hz)). The hemi-thioketal **13** was reduced by sodium borohydride in tetrahydrofuran to give a single diol (**14**) (ir 3450, 1740, and 1640 cm⁻¹) which was finally converted to dl-il-ludin M (**15**), mp 120–122.5°, by treatment with mercuric chloride in aqueous acetone. The infrared spectrum ((CCl₄) 3590, 3460, 1690, 1650, and 1605 cm⁻¹) and R_f values on tlc of the product were perfectly identical with those of the natural product in all respects.

Takeshi Matsumoto, Haruhisa Shirahama, Akitami Ichihara
Hyonsobb Shin, Shohei Kagawa, Fujio Sakan
Sojiro Matsumoto, Shuji Nishida
Department of Chemistry, Faculty of Science
Hokkaido University, Sapporo, Japan
Received March 25, 1968

Preparation and Structural Characterization of Six-Coordinate Iron(III) Complexes Containing the Fe–S–S Linkage

Sir:

Current interest in the structure–function relationship in nonheme iron proteins (NHIP) containing iron–sulfur bonds[1,2] has led us to investigate various aspects of the coordination chemistry of iron with sulfur donor ligands. One intriguing feature of certain NHIP is the presence of a sulfur atom, the so-called "inorganic" or

(1) A. San Pietro, Ed., "Non-Heme Iron Proteins: Role in Energy Conversion," Antioch Press, Yellow Springs, Ohio, 1965.
(2) R. Malkin and J. C. Rabinowitz, *Ann. Rev. Biochem.*, **36**, 113 (1967).

"acid-labile" sulfur, which is chemically distinct from cysteine sulfur and is required in a 1:1 mole ratio with iron in order for the protein to have biological activity. Two previously suggested alternative structural roles for this sulfur atom are (1) to link two or more iron atoms in linear chains[3] and (2) to participate in an iron-disulfide linkage with a sulfur atom from cysteine (cyst–S–S–Fe).[2] Although there is considerable precedent for sulfide-bridged metal atoms in inorganic chemistry, little information is available on metal–disulfide linkages.[4] The present note reports the preparation and structural characterization of six-coordinate iron complexes containing R–S–S–Fe bonds.

When tetrahydrofuran solutions containing Zn-(TTD)₂[5,6] were treated with ferric chloride dissolved in methanol, black crystals were obtained. After recrystallization from carbon disulfide–petroleum ether, analysis of the complex indicated the formula Fe-(TTD)₂(DTT).[6] *Anal.* Calcd for C₂₄H₂₁S₈Fe: C, 46.4; H, 3.38. Found: C, 46.7; H, 3.57. Treatment of chloroform solutions of this compound with triphenylphosphine[7] yielded, in addition to triphenylphosphine sulfide, complexes Fe(TTD)(DTT)₂ and Fe-(DTT)₃·CHCl₃. *Anal.* Calcd for C₂₄H₂₁S₇Fe: C, 48.9; H, 3.59. Found: C, 48.2; H, 3.58. Calcd for C₂₄H₂₁S₆Fe·CHCl₃: C, 44.3; H, 3.25. Found: C, 44.3; H, 3.41. All complexes were found to have room-temperature magnetic moments in the range expected for low-spin Fe(III), 2.2–2.5 BM, and display contact-shifted proton nmr spectra. The nmr spectrum of Fe(DTT)₃·CHCl₃ in CS₂ provided confirmatory evidence for the chloroform of solvation. The results of a detailed analysis of the spectral and magnetic properties of these compounds will be reported later; here we summarize the important structural features of the representative complex Fe(TTD)(DTT)₂, as determined by a single-crystal X-ray diffraction study.

Crystals of the mixed ligand complex were found to have Laue symmetry 2/m with lattice constants a = 18.24 ± 0.03, b = 7.64 ± 0.02, c = 24.11 ± 0.03 Å, β = 125.4 ± 0.1°. From the measured density, ρ = 1.42, and observed systematic absences, $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, the space group was ascertained to be P2₁/c with four molecules per unit cell. The density calculated on the basis of the formula C₂₄H₂₁S₇Fe is 1.43. Intensity data were collected by the equiinclination Weissenberg technique for successive layers $h0l$–$h6l$ using Cu Kα radiation. The visually estimated intensities were then corrected for absorption and LP effects, placed on a common scale by Wilson's method, and used to compute a three-dimensional Patterson map. Solution of the Patterson revealed the location of the iron and several sulfur atoms, which provided sufficient phasing for the complete structure determination in subsequent Fourier and least-squares refinement

(3) D. C. Blomstrom, E. Knight, Jr., W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci., U. S.*, **51**, 1085 (1964).
(4) J. Weiss, *Fortschr. Chem. Forsch.*, **5**, 635 (1966); J. Weiss and H. Neubert, *Z. Naturforsch.*, **21b**, 286 (1966).
(5) Abbreviations used in this paper are as follows: TTD = thio-*p*-toluoyl disulfide, CH₃C₆H₄CS₃⁻; DTT = dithio-*p*-toluate, CH₃-C₆H₄CS₂⁻; MNT = 1,2-dicyano-1,2-ethylenedithiol.
(6) J. P. Fackler, D. Coucouvanis, J. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, **90**, 2784 (1968). In this reference it is noted that "Zn(TTD)₂" shows variable sulfur content on titration with triphenylphosphine and may in fact contain some Zn(TTD)(DTT) or Zn(DTT)₂.
(7) D. Coucouvanis and J. P. Fackler, Jr., *ibid.*, **89**, 1346 (1967); J. P. Fackler, Jr., and D. Coucouvanis, *ibid.*, **89**, 1745 (1967).

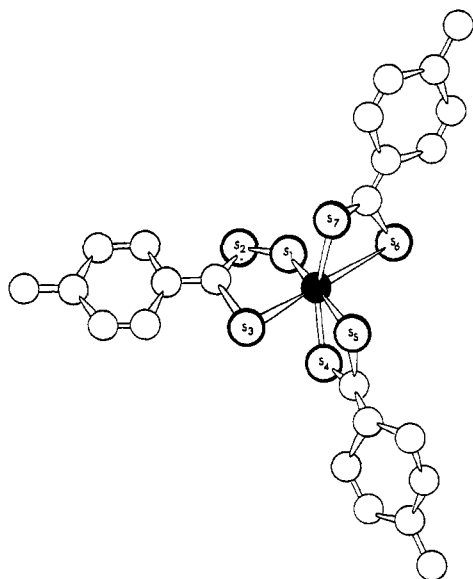Figure 1. Molecular structure of Fe(TTD)(DTT)$_2$. The iron atom is at the center and carbon atoms are not labeled.

calculations.[8] At present the conventional R factor[9] for isotropic refinement of all atoms is 0.096 for 1225 observed reflections.

The molecular structure of Fe(TTD)(DTT)$_2$ is shown in Figure 1. Selected bond lengths, angles, and other geometric features are summarized in Table I. The

Table I. Selected Geometric Features of Fe(TTD)(DTT)$_2$^{a,b}

Bond	Distance, Å	Interbond angle, deg	
Fe–S$_1$	2.19	S$_1$–Fe–S$_3$	92.8
Fe–S$_3$	2.23	S$_4$–Fe–S$_5$	73.9
Fe–S$_4$	2.29	S$_6$–Fe–S$_7$	73.8
Fe–S$_5$	2.33	S$_1$–S$_2$–C	111.7
Fe–S$_6$	2.35	S$_2$–C–S$_3$	121
Fe–S$_7$	2.31	S$_4$–C–S$_5$	113
S$_1$–S$_2$	2.09	S$_6$–C–S$_7$	110
Nonbonded			
Fe–S$_2$	3.44		
S$_1$–S$_3$	3.20		
S$_4$–S$_5$	2.78		
S$_6$–S$_7$	2.80		

^{a} Bond distances reported have individual estimated standard deviations of ±0.02 Å and interbond angles of ±0.4° (S–Fe–S) and ±1° (S–C–S). ^{b} See Figure 1 for atom-labeling scheme.

complex contains two four-membered chelate rings and one five-membered chelate ring, with six sulfur donor atoms coordinated to iron at the apices of a distorted octahedron. The geometry of the four-membered rings includes a mean Fe–S distance of 2.32 ± 0.02 Å, an average S–Fe–S angle of 73.8°, an average S–C–S angle of 111°, and an average "bite" distance of 2.79 ± 0.01 Å. These values are in general agreement with similar results obtained for other sulfur-coordinated iron complexes containing four-membered rings, Fe–

(8) Programs for the IBM 7094 computer used in this work, in addition to various local programs written at the Brookhaven National Laboratory and kindly made available to us, were Burnham's GNABS absorption program, Zalkin's FORDAP Fourier program, and the Busing–Levy ORFLS least-squares program and ORFFE error function program.

(9) Defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$.

$(NO)(S_2CN(CH_3)_2)_2$[10] and $FeCl(S_2CN(C_2H_5)_2)_2$.[11] The geometric features of the five-membered ring are quite different, however, with an average Fe–S distance of 2.21 ± 0.02 Å, a S–Fe–S angle of 92.8°, a S–C–S angle of 121°, and a S$\cdots$S bite of 3.20 Å. The values may be compared with the average Fe–S distance of 2.23 Å, S–Fe–S angle of 90°, and ligand bite distance of 3.15 Å recently found for $\{Fe(MNT)_2\}_2^{2-}$.[5,12] To a first approximation, therefore, the geometry of Fe(TTD)-(DTT)$_2$ may be understood in terms of the "normal" constraints imposed by the participation of the iron atom in both four- and five-membered chelate rings with sulfur donor atoms, quite apart from any effect which the electronic structure of the ligand molecules might have. Other geometric features, e.g., the near-planarity of the $CH_3C_6H_4CS_2$ groups and nonplanarity of the $CH_3C_6H_4CS_3$ ligand, may reflect the over-all electronic structure of the molecule as will be discussed in detail later.

The presence of Fe–S–S bonds in the present structure strongly supports the previous structural assignment for related "sulfur-rich" complexes of nickel[7] and zinc.[6] It also seems likely that such units occur in the more fully sulfurated iron complex mentioned above.

(10) M. Colapietro, A. Domenicano, L. Scaramuzza, A. Vaciago, and L. Zambonelli, Chem. Commun., 583 (1967); G. R. Davies, R. H. B. Mais, and P. G. Owston, ibid., 81 (1968).

(11) B. F. Hoskins, R. L. Martin, and A. H. White, Nature, 211, 627 (1966).

(12) W. C. Hamilton and I. Bernal, Inorg. Chem., 6, 2003 (1967).

Dimitri Coucouvanis, Stephen J. Lippard
*Department of Chemistry, Columbia University
New York, New York 10027*
Received March 11, 1968

Synthesis of *all-trans*-5,6-Dihydroretinal, a New Visual Chromophore

Sir:

We wish to report the synthesis of 5,6-dihydroretinal,[1] a new synthetic visual chromophore. To our knowledge, *this is the only polyene aldehyde outside of retinal and 3-dehydroretinal that has ever been found to combine with a visual protein.* The starting point in the multistep synthesis was 2,2,6-trimethylcyclohexanone (I) which itself was obtained from 2-carbethoxycyclohexanone.[2] Grignard reaction of I with chloromethyl ethyl ether followed by hydrolysis with 98% formic acid afforded[3] dihydrocyclocitral (II) in moderate over-all yield: bp 45–47° (0.5 mm); ir (neat): 2718 (ν_{CHO}), 1718 ($\nu_{C=O}$), 1450 (δ_{as-CH_3}), and 1380 cm^{-1} ($\delta_{s-gem-CH_3}$); mass spectrum, molecular ion at m/e 154; nmr: 1 H, doublet at τ 0.36 ($J = 4$ cps), 1 H, multiplet centered at 7.64, 1 H, multiplet centered at 8.09, 6 H, multiplet at 8.24–8.84, 3 H, singlet at 8.99, 6 H, closely spaced doublets at 9.02–9.10. Following a general procedure,[4]

(1) The name 5,6-dihydroretinal is adopted for this compound according to the IUPAC nomenclature for carotenoids. The systematic name for this compound is 9-(2,2,6-trimethylcyclohexyl)-3,7-dimethyl-2,4,6,8-nonatetraen-1-al.

(2) C. L. Stevens and A. J. Weinheimer, J. Am. Chem. Soc., 80, 4072 (1958).

(3) H. Normant and M. deBotton, Compt. Rend., 256, 1996 (1963).