

ring in a C_3 stereoisomer of the O_3MoZ^{3-} ion should be quite comparable with that which characterizes the averaged ring in the $O_3MoAMoO_3^{4-}$ complex. A pair of C_3 enantiomers that undergo sufficiently rapid intraconversion on the pmr time scale to give effective C_{3v} symmetry are the probable species in solution.

Table VI lists data that pertain to the atomic arrangement in crystals of $Na_4(O_3MoAMoO_3) \cdot 8H_2O$. The rather high stability of the crystalline phase, reflected in relatively small values of the effective thermal parameters for all of the atoms (Table II), is attributable to the efficient use of both the sodium ions and the water molecules in tying the bulky anions into the three-dimensional framework. A sodium ion of either structural class is surrounded by six oxygen atoms that delineate an irregular octahedron; Na–O distances range from 2.29 to 2.77 Å (Table VI). A sodium ion Na_{1+} coordinates one oxide-oxygen, two water-oxygen, and three carboxylate-oxygen atoms; the other sodium ion

Na_{2+} coordinates four water-oxygen and two carboxylate-oxygen atoms. Each carboxylate-oxygen atom that is not complexed to the Mo(VI) atom is coordinated to two sodium ions, one of each class, and every water molecule is coordinated to at least one sodium ion. The water molecules are also involved in hydrogen bonding (Table V) with carboxylate-oxygen and oxide-oxygen atoms. Separations between pairs of sodium ions range upward from 3.50 Å.

The crystalline arrangement may be described as layered along the a axis. A negatively charged layer of the type illustrated in Figure 3 consists of complex anions that are hydrogen bonded with and through water molecules. Such layers are interleaved by, and alternate with, puckered sheets of sodium ions. The description is quite formal because the layers and sheets have no clear planes of demarcation. Furthermore, the bonding between layer and sheet clearly is much stronger than it is within either layer or sheet.

The Crystal and Molecular Structure of Thio-*p*-toluoyldisulfidobis(dithio-*p*-toluato)iron(III)

Dimitri Coucouvanis and Stephen J. Lippard¹

Contribution from the Department of Chemistry, Columbia University, New York, New York 10027. Received August 19, 1968

Abstract: The crystal and molecular structure of thio-*p*-toluoyldisulfidobis(dithio-*p*-toluato)iron(III), $Fe(CH_3-C_6H_4CS_3)(CH_3C_6H_4CS_2)_2$, $Fe(TTD)(DTT)_2$, has been determined by a three-dimensional X-ray crystallographic analysis. The compound crystallizes as dark violet prisms in space group $P2_1/c$ with unit cell dimensions $a = 18.23$ (2), $b = 7.64$ (1), $c = 24.12$ (2) Å, $\beta = 125.4$ (1)°. The density of 1.43 g/cm³ calculated for four molecules per unit cell agrees well with the observed density of 1.42 ± 0.01 g/cm³. From approximately 1225 independent nonzero reflections estimated visually from Weissenberg photographs, the structure was solved by the use of conventional Patterson, Fourier, and least-squares refinement techniques to a final value of the discrepancy index, R , of 0.085. The geometry about the iron atom consists of a distorted octahedron of sulfur atoms contributed by two essentially equivalent bidentate dithioacid ligands and a third bidentate ligand containing an extra sulfur atom to form the structural grouping I, shown in the text. The average of four Fe–S distances in the four-membered rings is 2.32 ± 0.02 Å, whereas the two Fe–S distances in the five-membered ring are 2.18 and 2.24 ± 0.01 Å, respectively. These differences may be understood in terms of simple ring constraint and valence-bond resonance arguments. The S–S distance in the five-membered chelate ring is 2.09 ± 0.01 Å. An analysis of the geometry reveals some evidence for electron delocalization between the iron atom and the ligand molecules. A brief discussion of the possible relevance of this work to nonheme iron protein systems is set forth.

In recent years there has been a growing interest in a series of electron-transfer proteins containing sulfur-bound iron atoms in a nonheme environment.^{2,3} Of special interest is a class of nonheme iron proteins (NHIP) which is characterized by the presence of two or more iron atoms per mole of protein, relatively low redox potentials, a biologically unique form of sulfur which can be released as H_2S upon acidification (the so-called "acid-labile" sulfur), and bonds between the iron atoms and the mercaptide function of the amino acid cysteine. Examples include the plant and bacterial

ferredoxins.^{2,3}

The stability and unusual electronic properties of the sulfur-coordinated iron atoms in the ferredoxins appear to be related to the presence of the acid-labile sulfur, the nature of which has not yet been established. Two likely possibilities are either that this sulfur is present as sulfide, S^{2-} , and perhaps functions as a bridging ligand,⁴ or that the R–S–S–Fe linkages exist.³ Recent investigations in our laboratory⁵ have been designed to produce iron–sulfur complexes of possible relevance to ferredoxin systems in general and, in particular, to

(1) Fellow of the Alfred P. Sloan Foundation.

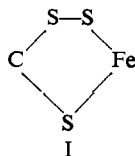
(2) A. San Pietro, Ed., "Non-Heme Iron Proteins: Role in Energy Conversion," Antioch Press, Yellow Springs, Ohio, 1965.

(3) (a) R. Malkin and J. C. Rabinowitz, *Ann. Rev. Biochem.*, **36**, 113 (1967); (b) R. W. Miller and V. Massey, *J. Biol. Chem.*, **240**, 1453 (1965).

(4) D. C. Blomstrom, E. Knight, W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci., U. S.*, **51**, 1085 (1964).

(5) (a) D. Coucouvanis and S. J. Lippard, *J. Am. Chem. Soc.*, **90**, 3281 (1968); (b) D. Coucouvanis, S. J. Lippard, B. G. Segal, and J. A. Zubieta, to be submitted for publication.

provide heretofore nonexistent information concerning the geometric and electronic structures of molecules containing iron-disulfide bonds. The present paper reports the details of a single-crystal X-ray structure determination of one such complex, $\text{Fe}(\text{TTD})(\text{DTT})_2$,⁶ which contains the structural grouping I.



Experimental Procedures and Results

Collection and Reduction of X-Ray Data. The compound was prepared as described elsewhere.⁶ The crystal used in all X-ray studies reported here was a small, violet, nearly rectangular parallelepiped of approximate dimensions $0.05 \times 0.13 \times 0.65$ mm. Clear fingernail polish was used to mount the crystal on the end of a glass fiber along the longest (b) axis. After an approximate optical alignment, the crystal was transferred to the precession and Weissenberg cameras where the space group and unit cell dimensions were determined using Ni-filtered $\text{Cu K}\alpha$ radiation (λ 1.5418 Å). The density was measured by accurately determining the weight (and thus the volume) of the degassed water displaced by a weighed amount of the complex. Intensity data were collected on the Weissenberg camera using copper radiation filtered through nickel. Approximately 1225 independent nonzero reflections, for which $\theta \leq 46^\circ$, were obtained from equininclination Weissenberg photographs $h0l$ - $h6l$ using the multiple-film technique. Each spot was compared with a scale prepared from timed exposures of one reflection from the same crystal.

In view of the nonspherical nature of the crystal and the relatively high linear absorption coefficient, $\mu = 96 \text{ cm}^{-1}$, absorption corrections were applied using Burnham's program.⁷ The transmission coefficients ranged from 0.42 to 0.60. In addition to absorption, the raw data, I , were corrected for the usual Lorentz and polarization effects and then placed on an approximate absolute scale through a modification of Wilson's method.⁷ From the resultant values for $|F_o|$ and $|F_c|^2$, the structure was solved by the usual Patterson, Fourier, and least-squares refinement processes (see below). Scattering factors for the zerovalent atoms were obtained from the "International Tables."⁸ Anomalous dispersion corrections were applied to the iron and sulfur atom form factors.⁹ Weights were assigned to each reflection in the least-squares process according to the following scheme: $\sigma = 20/I$ for $I \leq 20$; $\sigma = I/300$ for $I \geq 300$; $\sigma = 1$ for $20 < I < 300$,

(6) TTD = thio-*p*-toluoyl disulfide, $\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2^-$; DTT = dithio-*p*-toluate, $\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2^-$.

(7) Programs for the IBM 7094 used in this work include local versions of DATLST and DP3, the Brookhaven data list and film data processing programs, GNABS, the Burnham general absorption program for Weissenberg geometry, XDATA, the Brookhaven Wilson plot and scaling program, FORDAP, the Zalkin Fourier program, OR-FLS, the Busing-Martin-Lévy structure factor calculation and least-squares refinement program, OR-FFE, the Busing-Martin-Lévy error function program, and MGEOM, the Wood molecular geometry program.

(8) "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, pp 202, 204.

(9) Reference 8, p 213 ff.

where the weights w were taken as $1/\sigma^2$. Toward the end of the refinement, an empirical weighting scheme¹⁰ of the form $\sigma = (3.0 + 7.8 \times 10^{-3}|F_o| + 2 \times 10^{-4}|F_o|^2)$ was adopted, where again $w = 1/\sigma^2$.

Unit Cell and Space Group. The complex $\text{Fe}(\text{TTD})(\text{DTT})_2$ crystallizes in the monoclinic system with $a = 18.23 \pm 0.02$, $b = 7.64 \pm 0.01$, $c = 24.12 \pm 0.02$ Å, and $\beta = 125.4 \pm 0.1^\circ$. The cell volume ($V = 2739$ Å³) and density ($\rho = 1.42 \pm 0.1 \text{ g/cm}^3$) require four formula weights per unit cell. The calculated density, 1.43 g/cm^3 , agrees well with that observed. From the observed extinctions, $h0l$, $l \neq 2n$, and $0k0$, $k \neq 2n$, the probable space group is $P2_1/c$.¹¹ All atoms occupy the general fourfold set of positions (4c): $\pm(x, y, z)$ and $\pm(x, 1/2 - y, 1/2 + z)$.

Determination of the Structure. Using the corrected data, an origin-removed, sharpened Patterson map was computed⁷ and solved for the position of the iron atom. A difference Fourier map was then prepared with the signs of the structure factors assigned on the basis of the trial positional parameters for the iron atom. Careful examination of the Fourier map and Patterson synthesis led to the location of three sulfur atoms which, when used along with the iron atom to phase a second difference Fourier, revealed the remaining four sulfur atoms. Subsequent cycles of least-squares refinement of positional and isotropic thermal parameters, structure factor calculation, and Fourier synthesis produced positional parameters for the remaining 24 nonhydrogen atoms in the asymmetric unit. Refinement of these parameters and isotropic temperature factors converged at values of 0.096 and 0.110 for the discrepancy factors, $R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2 / \Sigma w F_o^2)^{1/2}$, respectively. At this stage, a difference Fourier map showed nonisotropic motion for the iron and seven sulfur atoms. Refinement was therefore continued in which anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were assigned to the iron and sulfur atoms, and isotropic temperature factors to the remaining 24 carbon atoms. After two such refinement cycles and using the empirical weighting scheme, R_1 was 0.085 and R_2 , 0.119. The standard deviation of an observation of unit weight¹⁰ was 1.69. A final difference Fourier showed no peaks greater than $0.8 \text{ e}/\text{Å}^3$, on a scale where the average value for a carbon atom is $4.0 \text{ e}/\text{Å}^3$. No attempt was made to locate the hydrogen atoms.

The atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the last least-squares refinement cycle,¹² are given in Table I. The root-mean-square amplitudes of vibration derived from the iron and sulfur atom thermal parameters are presented in Table II. A perspective drawing of the molecule showing the atom-labeling scheme appears in Figure 1.

(10) D. W. J. Cruickshank in "Computing Methods of Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, N. Y., 1965, pp 112-115.

(11) Reference 8, Vol. I, p 99.

(12) A compilation of observed and calculated structure factor amplitudes has been deposited as Document No. NAPS-00140 with the ASIS National Auxiliary Publication Service, % CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. Copies may be secured by citing the document number and remitting \$1.00 for microfiche or \$3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS-NAPS.

Table I. Final Positional and Thermal Parameters for $\text{Fe}(\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2)(\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2)_2^{a,b}$

Atom	X	Y	Z	B, Å ²
Fe	-0.1833 (2)	0.0785 (3)	0.1596 (2)	c
S1	-0.0389 (4)	0.0701 (6)	0.2392 (3)	c
S2	0.0276 (4)	0.1078 (7)	0.1931 (3)	c
S3	-0.1630 (3)	0.1675 (6)	0.0809 (3)	c
S4	0.1941 (3)	0.2868 (6)	0.3672 (3)	c
S5	-0.3337 (3)	0.0302 (6)	0.0703 (3)	c
S6	-0.2111 (4)	0.0295 (7)	0.2418 (3)	c
S7	-0.2219 (4)	0.3447 (6)	0.1798 (3)	c
C1	-0.053 (1)	0.166 (2)	0.111 (1)	3.9 (4)
C2	-0.024 (1)	0.207 (2)	0.067 (1)	4.2 (4)
C3	0.063 (1)	0.280 (2)	0.095 (1)	5.6 (5)
C4	0.089 (1)	0.322 (3)	0.051 (1)	6.3 (5)
C5	0.035 (1)	0.280 (2)	-0.016 (1)	5.8 (5)
C6	0.062 (2)	0.178 (3)	0.431 (1)	7.4 (6)
C7	-0.051 (1)	0.289 (3)	0.453 (1)	6.2 (6)
C8	-0.081 (1)	0.171 (2)	-0.004 (1)	5.7 (5)
C9	-0.300 (1)	-0.179 (2)	0.070 (1)	4.5 (4)
C10	-0.363 (1)	-0.308 (2)	0.018 (1)	4.8 (4)
C11	-0.324 (1)	-0.469 (2)	0.015 (1)	5.3 (5)
C12	-0.382 (1)	-0.593 (2)	-0.034 (2)	5.9 (5)
C13	-0.475 (2)	-0.562 (3)	-0.076 (1)	6.3 (5)
C14	0.461 (2)	0.205 (3)	0.372 (1)	8.0 (7)
C15	0.513 (1)	0.405 (2)	0.074 (1)	6.1 (5)
C16	-0.457 (1)	-0.274 (2)	-0.026 (1)	5.7 (5)
C17	-0.236 (1)	0.242 (2)	0.236 (1)	4.8 (5)
C18	-0.270 (1)	0.331 (3)	0.272 (1)	6.3 (5)
C19	-0.263 (1)	0.513 (3)	0.279 (1)	6.4 (6)
C20	-0.294 (1)	0.601 (3)	0.314 (1)	6.1 (5)
C21	-0.325 (2)	0.498 (4)	0.345 (2)	9.5 (8)
C22	0.356 (2)	0.094 (4)	0.111 (2)	12 (1)
C23	-0.330 (2)	0.320 (5)	0.341 (2)	11 (1)
C24	-0.299 (2)	0.228 (4)	0.305 (1)	9.5 (8)

Anisotropic Temperature Factors^d ($\times 10^3$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	5.9 (2)	18 (2)	3.4 (2)	0.6 (3)	2.6 (1)	0.7 (2)
S1	6.8 (4)	26 (2)	3.4 (2)	0.8 (5)	2.3 (3)	1.3 (4)
S2	5.4 (3)	33 (2)	3.0 (2)	1.8 (5)	2.0 (2)	0.0 (4)
S3	5.9 (3)	22 (2)	3.1 (2)	1.2 (4)	2.4 (2)	1.6 (4)
S4	5.1 (3)	19 (2)	3.5 (2)	-1.4 (4)	1.9 (2)	-0.7 (4)
S5	5.5 (3)	19 (2)	4.0 (3)	1.6 (4)	2.6 (2)	1.1 (4)
S6	7.8 (4)	25 (2)	3.7 (3)	2.5 (5)	3.1 (3)	2.6 (4)
S7	7.1 (4)	19 (2)	3.7 (2)	1.2 (5)	3.0 (2)	0.6 (4)

^a Standard deviations, in parentheses beside each entry, occur in the last significant figure for each parameter. ^b The atom-labeling system used refers to that of Figure 1. ^c Atom refined anisotropically. ^d The form of the anisotropic ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

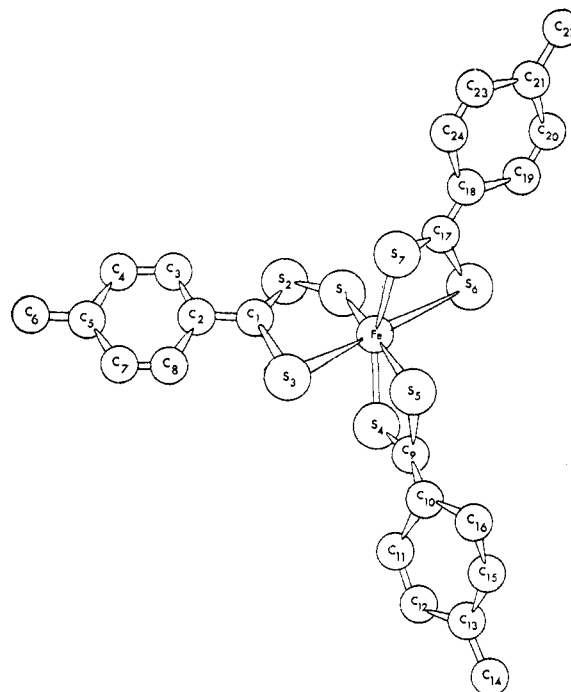
Table II. Root-Mean-Square Amplitudes of Vibration (in Å)^a for Iron and Sulfur Atoms in $\text{Fe}(\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2)(\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2)_2$

Atom	Minimum	Intermediate	Maximum
Fe	0.229	0.259	0.262
S ₁	0.244	0.285	0.300
S ₂	0.235	0.259	0.321
S ₃	0.225	0.261	0.275
S ₄	0.219	0.252	0.290
S ₅	0.221	0.260	0.292
S ₆	0.233	0.288	0.312
S ₇	0.231	0.265	0.285

^a Taken along the principal axes of the thermal ellipsoids. The orientations of these axes may be worked out from the data of Table I and the unit cell parameters.

Discussion

The Crystal and Molecular Structure. The crystal structure defined by the unit cell dimensions, symmetry operations, and parameters of Table I consists of monomolecular $\text{Fe}(\text{TTD})(\text{DTT})_2$ units. The basic coordi-

**Figure 1.** Molecular structure of $\text{Fe}(\text{TTD})(\text{DTT})_2$ showing the atom-labeling scheme.

nation polyhedron about the iron atom is a distorted octahedron with six sulfur atoms, two from each ligand molecule, at the apices (Figure 1). There are two four-membered chelate rings and one five-membered chelate ring. The presence of the five-membered ring strongly supports the previous structural assignments made for related complexes of nickel and zinc.¹³ As evident from Figure 1, the molecule has no symmetry. Optical isomerism is therefore a possibility, but the centrosymmetric space group accommodates an equimolar, racemic mixture of the two enantiomorphs.

Selected features of the geometry of the inner coordination group are summarized in Table III, from which

Table III. Geometry of the Inner Coordination Group. Selected Interatomic Distances (Å) and Angles (degrees) about the Iron and Sulfur Atoms^{a,b}

Interatomic distance		Angle	
Fe-S ₁	2.184 (7)	S ₁ -Fe-S ₃	92.6 (2)
Fe-S ₂	3.449 (7)	S ₂ -S ₁ -Fe	107.8 (3)
Fe-S ₃	2.238 (7)	S ₄ -Fe-S ₅	74.0 (2)
Fe-S ₄	2.297 (5)	S ₆ -Fe-S ₇	73.7 (2)
Fe-S ₅	2.336 (6)	S ₁ -Fe-S ₅	168.6 (2)
Fe-S ₆	2.343 (7)	S ₃ -Fe-S ₆	171.3 (2)
Fe-S ₇	2.296 (6)	S ₄ -Fe-S ₇	158.9 (3)
S ₁ -S ₂	2.086 (8)	S ₁ -Fe-S ₄	94.7 (2)
S ₁ -S ₃	3.199 (8)	S ₁ -Fe-S ₆	89.7 (2)
S ₂ -S ₃	2.953 (8)	S ₁ -Fe-S ₇	101.6 (3)
S ₄ -S ₅	2.787 (6)	S ₃ -Fe-S ₄	94.9 (2)
S ₅ -S ₇	2.780 (7)	S ₃ -Fe-S ₅	87.1 (2)
		S ₃ -Fe-S ₇	97.6 (2)
		S ₄ -Fe-S ₆	93.3 (2)
		S ₃ -Fe-S ₆	92.3 (2)
		S ₅ -Fe-S ₇	89.7 (2)

^a See Figure 1 for atom-labeling scheme. ^b Numbers in parentheses are estimated standard deviations.

(13) J. P. Fackler, Jr., D. Coucouvanis, J. A. Fetchin, and W. C. Seidel, *J. Am. Chem. Soc.*, 90, 2784 (1968), and references contained therein.

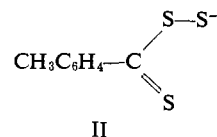
departures from the idealized O_h symmetry may be seen. The two crystallographically and chemically independent Fe-DTT chelate rings are structurally very similar. The four Fe-S bond distances in these rings occur in two groups, the Fe-S₄ and Fe-S₇ distances of 2.296 ± 0.006 and 2.297 ± 0.005 Å, respectively, and the Fe-S₅ and Fe-S₆ distances of 2.336 ± 0.006 and 2.343 ± 0.007 Å, respectively. The average bond length difference between these groups, 0.043 Å, is approximately six times as large as the estimated standard deviation in an individual bond length and is therefore probably significant. The longer pair of bonds, Fe-S₅ and Fe-S₆, are approximately coplanar with the best plane through the five-membered chelate ring (Figure 1). One possible explanation for the lengthening of these bonds is that charge delocalization (back-bonding) might occur more effectively to the TTD ring than to the DTT rings. This would increase the bond order of the Fe-S₁ and Fe-S₃ bonds at the expense of the bonds to S₅ and S₆.

The average geometric features of the four-membered chelate rings (Table III) compare favorably with similar results obtained for iron dithiocarbamate complexes. In $\text{Fe}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2\text{Cl}$, for example, the reported¹⁴ Fe-S distance (av) is 2.32 Å and in $\text{Fe}[(\text{C}_2\text{H}_5)_2\text{NCS}_2]_2\text{NO}$,¹⁵ ~ 2.29 Å. The latter complex is found¹⁵ to have S-Fe-S angles of 76.0° and a (calculated) S...S "bite" of 2.82 Å. Similar trends are observed to occur in certain structurally characterized nickel compounds containing dithioacetamide,¹⁶ ethyl xanthate,¹⁷ or trithiocarbonate¹⁸ as ligands. Here the metal-sulfur bond distances tend to be smaller, ~ 2.22 – 2.24 Å, presumably because of the smaller covalent radius of nickel. Also noteworthy is a recent structural characterization of bis(dithiobenzoato)palladium(II) in which Pd-S distances of 2.32–2.34 Å, S-Pd-S angles of 74.4 – 74.7° , and a S...S bite of 2.82 Å were found.¹⁹

As evident from Table III, the coordination geometry of the five-membered Fe-TTD chelate ring is quite different from that of the two Fe-DTT rings. In fact, the present complex offers a unique opportunity to compare the structural features of these two types of ring systems within the same molecule. In the five-membered ring, the average Fe-S distance has shortened to 2.21 ± 0.02 Å (rms error) and the S₁-Fe-S₃ angle is $92.6 \pm 0.2^\circ$, reflecting the greater degree of metal-ligand overlap possible when the ring size permits a normal, octahedral angle at the iron atom. The S₂...S₃ distance is ~ 0.16 Å larger than the corresponding distances in the DTT rings, again in the direction expected from ring strain arguments. Unfortunately, no other iron-sulfur complex with a five-membered ring formed by the metal and a mononegative chelate ligand anion has been structurally characterized, so a relevant comparison to the present Fe-TTD system is not possible. Two structures of 1,2-dicyano-1,2-ethylene-dithiol iron complexes are known,^{20,21} however, for

which Fe-S distances of 2.23 and 2.27 Å and S-Fe-S angles of $\sim 90^\circ$ have been reported.

Further examination of the Fe-TTD ring reveals several interesting features. First, there is a significant (8σ) difference between the Fe-S₁ bond distance of 2.184 ± 0.007 Å and the Fe-S₃ bond length, 2.238 ± 0.007 Å. Since the most favorable resonance form not involving the aromatic ring which can be written for the ground state of the free ligand anion is II, it is



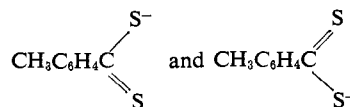
not unreasonable to attribute this difference in iron-sulfur bond lengths to the greater coordinating ability of a sulfido function over a thioketone.²² Another structural feature of interest in the Fe-TTD ring is the S₁-S₂ bond length, 2.086 ± 0.008 Å. This value approximates the average value of 2.05 ± 0.01 Å quoted²³ for a number of compounds containing sulfur-sulfur bonds. Two coordination compounds with chelate rings in which a sulfur-sulfur bond occurs are $[\text{Pd}(\text{NS}_2)_2]$ ²⁴ and $(\text{NH}_4)_2[\text{Pt}(\text{S}_2)_3] \cdot 2\text{H}_2\text{O}$.²⁵ The average S-S distances in these complexes are 1.95 and 2.05 Å, respectively. At present we attach no special significance to the somewhat larger S-S bond length in $\text{Fe}(\text{TTD})(\text{DTT})_2$. The S₂-S₁-Fe angle of $107.8 \pm 0.3^\circ$ correlates well with the average S-S-Pd angle of 104.0° and S-S-Pt angle of 109.4° reported previously.^{24,25} A best plane calculation⁷ through the Fe, S₂, C₁, S₃ atoms shows them to lie within 0.02 Å of a common plane. The distance of S₁ from this plane is 0.23 Å, which reflects the slight degree of puckering of the five-membered Fe-TTD chelate ring.

Selected geometric features of the two DTT ligands and the $\text{CH}_3\text{C}_6\text{H}_4\text{CS}_2$ portion of the TTD ligand are presented in Table IV. As can be judged from the table, the bond distances and angles within the three aromatic rings are normal and the carbon atoms are within at least 0.03 Å of being coplanar. The six crystallographically independent C-S distances are in fact chemically identical, the average value of 1.69 Å (rms error, 0.02 Å) being nearly equal to the corresponding value in $(\text{C}_6\text{H}_5\text{CS}_2)_2\text{Pd}$, 1.70 ± 0.01 Å.¹⁹ The average S-C-S angle of $111.5 \pm 0.5^\circ$ in the DDT ligands is also comparable to the value of 112.5° found¹⁹ for the palladium complex, but smaller than the 121° angle which occurs in the less constrained, five-membered Fe-TTD ring. Noteworthy also is the average C-CS₂ bond length for the three ligands, 1.48 ± 0.02 Å,

(20) A. I. M. Rae, *ibid.*, 1245 (1967).

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

(22) Such cannot of course be the case for the Fe-DTT rings discussed above since both



resonance structures contribute equally in the free ligand anions.

(23) L. E. Sutton, Ed., "Tables of Interatomic Distances and Configurations in Molecules and Ions," Supplement 1956-1959, Special Publication No. 18, The Chemical Society, London, 1965, p S11s.

(24) J. Weiss, *Fortschr. Chem. Forsch.*, 5, 635 (1966); J. Weiss and H. Neubert, *Z. Naturforsch.*, 21b, 286 (1966).

(25) P. E. Jones and L. Katz, *Chem. Commun.*, 842 (1967).

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

(15) 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).

(16) L. Capacchi, M. Nardelli, and A. Villa, *ibid.*, 441 (1966).

(17) M. Franzini, *Z. Krist.*, 118, 393 (1963).

(18) J. S. McKechnie, S. L. Miesel, and I. C. Paul, *Chem. Commun.*, 152 (1967).

(19) M. Bonamico and G. Dessy, *ibid.*, 483 (1968).

Table IV. Selected Geometric Features of the DTT Ligand and the CH₃C₆H₄CS₂ Portion of the TTD Ligand^a

C-C (aromatic)			Bond distances, Å				Ligand ^b
Min	Max	Mean	C-S		C-CS ₂	C-CH ₃	
1.36 (3)	1.47 (3)	1.42 (3)	1.70 (2), 1.69 (3)		1.47 (3)	1.64 (3)	A
1.40 (2)	1.44 (2)	1.42 (2)	1.65 (2), 1.71 (3)		1.48 (2)	1.56 (3)	B
1.36 (5)	1.46 (5)	1.41 (3)	1.67 (2), 1.71 (2)		1.49 (3)	1.63 (5)	C

C-C-C (aromatic)			Bond angles, deg			Ligand ^b
Min	Max	Mean ^c	S-C-S	S-C-C	C-C-CH ₃	
118 (2)	123 (2)	120	121 (1)	118 (1), 122 (1)	123 (2), 114 (2)	A
118 (1)	122 (2)	120	112 (1)	127 (1), 121 (1)	119 (2), 118 (2)	B
118 (3)	123 (3)	120	111 (1)	124 (1), 125 (1)	119 (3), 117 (3)	C

Best Planes^d

Best plane equation through ligand ring A 0.3628X - 0.9164Y + 0.1692Z = -1.725			
Distances (in Å) of carbon atoms from plane			
C ₂ 0.000	C ₄ -0.030	C ₆ 0.001	C ₈ -0.002
C ₃ 0.016	C ₅ 0.024	C ₇ -0.008	

Best plane equation through ligand ring B -0.615X - 0.4072Y + 0.6752Z = 5.415			
Distances (in Å) of carbon atoms from plane			
C ₁₀ 0.010	C ₁₂ -0.027	C ₁₄ 0.028	C ₁₆ -0.003
C ₁₁ 0.007	C ₁₃ 0.002	C ₁₅ -0.017	

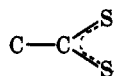
Best plane equation through ligand ring C 0.5489X - 0.0597Y + 0.8338Z = -0.461			
Distances (in Å) of carbon atoms from plane			
C ₁₈ -0.021	C ₂₀ -0.019	C ₂₂ 0.018	C ₂₄ 0.023
C ₁₉ 0.027	C ₂₁ -0.012	C ₂₃ -0.016	

^a See Figure 1 for atom-labeling scheme; numbers given in parentheses refer to the esd (or rms error in the case of averaged values) in the last significant figure listed. ^b Ligand A is the TTD group, ligand B contains S₄, S₅, and C₉-C₁₆, and ligand C contains S₆, S₇, and C₁₇-C₂₄. ^c The mean value of 120° is required by geometry since the rings are nearly planar. ^d Weighted least-squares planes were calculated with reference to an orthogonal coordinate system in which the Y axis is taken to be coincident with the cell b axis, the Z axis is in the direction $\vec{a} \times \vec{b}$, and the X axis is chosen according to the right-hand rule.

a value which suggests the possibility of π -electron delocalization between the *p*-toluoyl and CS₂ groups. A similar shortening of C-C bond distances (1.46-1.47 Å) was found in (C₆H₅CS₂)₂Pd and ascribed to partial double-bond character.¹⁹ Unlike the palladium compound, however, the ligands in Fe(DTT)(TTD)₂ are not strictly coplanar. In particular, each of the three aromatic rings is rotated about the C-CS₂ bond axis giving rise to dihedral angles²⁶ of 11.6 and 16.6° for the DTT ligands, and 30.2° for the TTD ligand. A likely, if hard to prove, source for nonplanarity of the ligands is crystal-packing forces, which are probably more severe in the present structure than in the planar, stacked (C₆H₅CS₂)₂Pd compound.

Possible Biological Relevance. The structural characterization of Fe(TTD)(DTT)₂ reported above demonstrates, to our knowledge for the first time, the existence of the Fe-S-S-R linkage. The possibility that similar structural units occur in NHIP has been previously considered,³ although no prototypes were then

(26) Calculated between the plane of the aromatic ring (Table IV) and the plane of the



atom grouping.

known. To the extent that small geometrical differences reflect varying degrees of charge delocalization, the present structure suggests that the TTD ligand is more effective in removing charge from the iron atom than the DTT ligands. This conclusion, if correct, is of interest since only in the presence of π -acceptor ligands such as carbonyl²⁷ or nitrosyl²⁸ have stable sulfide- and mercaptide-bridged iron complexes been isolated. These dimeric or oligomeric units have often been suggested to occur in NHIP such as the ferredoxins. Apart from these comments, the structure of Fe(TTD)(DTT)₂ provides no obvious insights into the ferredoxin systems, since dithioacid functional groups are not found among the amino acids. A comparison of certain other physical properties of Fe(TTD)(DTT)₂ and related complexes with those of the enzyme systems will be taken up later.^{5b}

Acknowledgments. We wish to thank the National Science Foundation for financial support of this research under Grant GP-6758, the Columbia University Computer Center for its cooperation, and Professor J. P. Fackler for helpful discussions and his interest in this work.

(27) R. B. King, *J. Am. Chem. Soc.*, **85**, 1584 (1963); C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(28) J. T. Thomas, J. H. Robertson, and E. G. Cox, *Acta Cryst.*, **11**, 599 (1958); G. Johansson and W. N. Lipscomb, *ibid.*, **11**, 594 (1958).