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Preparation and Structure of a Tetrameric Cyclopentadienyliron Sulfide, $[C_5H_5FeS]_4$

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The reaction of $[C_5H_5Fe(CO)_2]_2$ with cyclohexene sulfide has given, in addition to other organometallic products, a relatively insoluble, air-stable, black crystalline solid of formula $[C_5H_5FeS]_4$. Its structural characterization as a tetrameric complex was ascertained from a three-dimensional X-ray examination which showed $[C_5H_5FeS]_4$ to form monoclinic crystals with four molecules in a unit cell of symmetry C2/c and of dimensions a = 18.80 A, b = 7.68 A, c = 15.07 A, β = 109° 5′. A full-matrix least-squares refinement of the nonhydrogen atoms yielded final discrepancy values of 7.8 and 8.1% for the unweighted R_1 and weighted R_2 factors, respectively. The tetrameric structure can be viewed as formed from two interpenetrating distorted tetrahedra of iron and sulfur atoms; each iron of identical environment is coordinated to a π-cyclopentadienyl ring, *three* sulfur atoms, and *one* iron atom. With the assumption of cylindrical symmetry for each cyclopentadienyl ring the molecular configuration possesses tetragonal D_{2d} symmetry. A stereochemical consequence of each iron atom attaining a closed-shell electronic configuration by the formation of only one iron–iron bond is a symmetrical deformation of the molecule from an idealized cubic configuration of T_d symmetry (*with* or *without six* metal–metal bonds) to the observed configuration of lower tetragonal symmetry (containing two metal–metal bonds). As a result of a crystallographic twofold axis passing through the molecule, the Fe_4S_4 fragment contains one independent Fe–Fe bond of 2.650 A, four chemically equivalent independent Fe–S bonds of 2.204 A (av), and two other chemically equivalent independent Fe–S bonds of 2.250 A (av). The Fe–Fe bond in each of the two identical Fe_2S_2 fragments is also responsible for the symmetrical electron-pair Fe–S bridge bonds possessing a sharp Fe–S–Fe angle of 74° (av). The detailed molecular features are compared to those of related molecular complexes.

Introduction

Although a wide variety of metal carbonyl chalcogenides have been prepared[2–8] for which X-ray diffraction studies[9–12] have shown unusual configurations with new types of bonding, cyclopentadienylmetal sulfides are as yet unreported. This paper presents the synthesis and characterization by a single crystal X-ray analysis of the first such compound, $[C_5H_5FeS]_4$.[13]

Experimental Section

Preparation and Properties.—Cyclopentadienyliron dicarbonyl dimer (8.0 g, 22.6 mmoles) and cyclohexene sulfide (6.0 g, 41.1 mmoles) were heated under nitrogen in refluxing benzene for 4.5 hr. Filtration of the resulting black mixture followed by partial evaporation of the solvent led to precipitation of a black crystalline air-stable solid, which was recrystallized from a chloroform-octane mixture. Since the product slowly decomposed in solution and tended to separate out as a powder, it was rather difficult to get pure material. Several other products which were isolated from the filtrate by chromatographic separation will be discussed in a later paper.[14]

Anal. Calcd for C_5H_5FeS: C, 39.2; H, 3.3; S, 20.9; Fe, 36.6. Found:[15] C, 39.0; H, 3.9; S, 21.1; Fe, 36.1. The infrared spectrum of $[C_5H_5FeS]_4$ as a Nujol null, taken on a Perkin-Elmer Model 421 grating spectrometer with NaCl plates, shows absorption bonds at 2950 (w), 2930 (m), 2850 (w), 1730 (w), 1417 (m), 1194 (w), 1005 (w), 1000 (vw), 828 (vw), 805 (vw), and 707 (vw) cm^{-1}.

Single Crystal X-Ray Data.—Although oscillation photographs of crystals mounted about the b axis did not reveal any indications of twinning, zero- and upper-level Weissenberg photographs of a number of crystals showed extra reflections characteristic of a twinning on the (100) plane. Several recrystallizations of the compound from chloroform solution finally yielded a tiny untwinned needle crystal (of length 0.22 mm and average width 0.07 mm) which was used to collect the intensity data. The lattice cell parameters were determined from $hk0$ and $0kl$ precession photographs. Multiple-film equiinclination Weissenberg data were obtained for reciprocal levels $h0l$ through $h8l$ with zirconium-filtered Mo Kα radiation. The intensities of 582 independent diffraction maxima were visually estimated and then corrected for Lorentz-polarization effects. Since the estimated $\mu R_{\max}$ value was only 0.15, absorption corrections were not applied. The variable weights of the observed structure factor amplitudes utilized in the least-squares refinement were assigned as follows: $\sqrt{w} = 20/F_o$ if $I_0 \geq 4I_0(\min)$, $\sqrt{w} = 1.25 \cdot I_0^2/F_oI_0(\min)^2$ if $I_0 < 4I_0(\min)$.

Unit Cell and Space Group.—The crystals of $[C_5H_5FeS]_4$ are monoclinic with lattice parameters $a = 18.80 \pm 0.03$ A, $b = 7.68 \pm 0.01$ A, $c = 15.07 \pm 0.03$ A, $\beta = 109° 5' \pm 20'$; the volume of the unit cell is 2056 A^3; $\rho_{\text{calcd}} = 1.98$ g cm^{-3} for four tetramers per unit cell. The total number of electrons per unit cell, $F(000)$, = 1232. Systematic absences of $h + k = 2n + 1$ for $\{hkl\}$ and $l = 2n + 1$ for $\{h0l\}$ indicate the probable space groups Cc (C_s^4) and C2/c (C_{2h}^6), of which the latter centrosymmetric one was later confirmed by the structural refinement. All crystallographically independent atoms were found to occupy the general eightfold set of positions (8f): $(0, 0, 0;\ ^1/_2, ^1/_2, 0) \pm (x, y, z;\ x, -y, ^1/_2 + z)$.[16]

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[10] C. H. Wei and L. F. Dahl, *ibid.*, **4**, 1 (1965).

[11] C. H. Wei and L. F. Dahl, *ibid.*, **4**, 493 (1965).

[12] C. H. Wei and L. F. Dahl, Abstracts of Papers, National Meeting of the American Crystallographic Association, Montana State College, Bozeman, Mont., July 1964; to be published.

[13] Before the single crystal X-ray study was begun, this compound was believed to be a hexanuclear iron complex on the basis of preliminary analytical data. The correct formulation as a tetrameric species of the above composition was shown from the X-ray work and verified by subsequent elemental analysis.

[14] P. M. Treichel, G. R. Wilkes, and M. Brauner, to be published.

[15] Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[16] "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1952, p 101.

Determination of the Structure.—A careful examination of a three-dimensional Patterson function computed[17] from the corrected intensities finally provided a complete interpretation of all *intra-* and *inter*molecular Fe–Fe and Fe–S vectors on the basis of the space group C2/c. These vectors indicated an Fe_4S_4 molecular fragment in which two irregularly shaped tetrahedra, one composed of four iron and the other of four sulfur atoms, interpenetrate such that each sulfur is bonded to three iron atoms and each iron is bonded to one iron and three sulfur atoms. Approximate positional parameters were obtained for the two independent iron atoms, Fe_1 and Fe_2, and the two independent sulfur atoms, S_3 and S_4, of the Fe_4S_4 fragment which possesses a crystallographic twofold axis. Two cycles of a block-diagonal least-squares isotropic refinement[18] of the derived Patterson coordinates were carried out in which initial thermal parameters based on related structures[9–12] were arbitrarily assumed for the iron and sulfur atoms. The resulting value of 19% for the unweighted discrepancy factor, $R_1 = [\Sigma||F_o| - |F_c||/\Sigma|F_o|] \times 100$, indicated the correctness of the Fe_4S_4 model. Subsequent three-dimensional Fourier syntheses[17] located the ten carbon atoms of the two independent cyclopentadienyl rings.

A block-diagonal isotropic least-squares refinement[18] of all fourteen nonhydrogen atoms lowered the R_1 value to 10.0%, after which a full-matrix least-squares program[19] with individual atomic temperature factors and with nine interlayer scale factors was utilized for further refinement. At the end of three cycles R_1 and $R_2 = [\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2} \times 100$ stood at 7.8 and 8.1%, respectively; all parameter shifts were less than 8% of their individual standard deviations. In the structure factor calculations the scattering factors used for iron were those of Thomas and Umeda,[20] for sulfur those of Dawson,[21] and for carbon those of Berghuis, *et al.*[22] A three-dimensional difference Fourier map based on the output parameters of the last cycle (given in Table I) showed no anomalies. No attempt was made to locate the positions of the hydrogen atoms.

TABLE I

ATOMIC PARAMETERS WITH STANDARD DEVIATIONS[a]

Atom	x ($10^4\sigma_x$)	y ($10^4\sigma_y$)	z ($10^4\sigma_z$)	B ($10^2\sigma_B$)
Fe_1	0.4294 (2)	0.4339 (4)	0.1473 (2)	3.18 (11)
Fe_2	0.4148 (2)	0.1902 (4)	0.2645 (2)	3.06 (11)
S_3	0.4448 (4)	0.4648 (7)	0.2976 (5)	3.27 (15)
S_4	0.4629 (4)	0.1588 (8)	0.1495 (4)	3.47 (15)
C_5	0.3702 (13)	0.4300 (33)	−0.0036 (15)	4.14 (53)
C_6	0.4197 (14)	0.5856 (33)	0.0260 (17)	5.31 (60)
C_7	0.3791 (13)	0.6829 (35)	0.0921 (16)	4.82 (58)
C_8	0.3323 (13)	0.5942 (30)	0.1055 (16)	4.06 (52)
C_9	0.3167 (14)	0.4451 (35)	0.0490 (17)	5.09 (60)
C_{10}	0.3733 (13)	−0.0592 (28)	0.2834 (16)	4.02 (50)
C_{11}	0.3232 (13)	0.0259 (31)	0.2005 (17)	4.40 (54)
C_{12}	0.2919 (13)	0.1779 (32)	0.2288 (17)	4.29 (52)
C_{13}	0.3253 (13)	0.2038 (30)	0.3282 (17)	4.09 (51)
C_{14}	0.3736 (14)	0.0607 (35)	0.3604 (17)	4.89 (56)

[a] Standard deviations of last significant figures are given in parentheses.

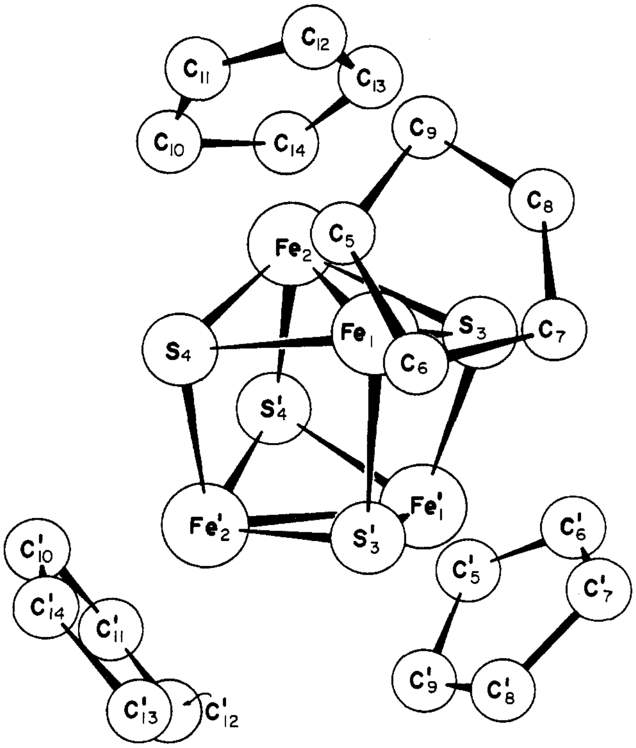

Figure 1.—Molecular configuration of $[C_5H_5FeS]_4$.

A listing of the observed and calculated structure factors based on these atomic parameters is shown in Table II. The interatomic distances and bond angles calculated with the Busing–Martin–Levy function and error program[23] are tabulated in Tables III and IV, respectively. Standard deviations obtained from the full inverse matrix also include the estimated lattice constant errors. Table V gives the "best" molecular planes formed by certain atoms and the distances of these and other atoms from the planes obtained by a least-squares method with the Smith program.[24]

Results and Discussion

Crystalline $[C_5H_5FeS]_4$ is composed of tetrameric molecules with the configuration depicted in Figure 1. Each iron atom of similar localized environment is coordinated to a π-cyclopentadienyl ring, three sulfur atoms, and one iron atom such that it attains a closed-shell electronic configuration. With the assumption of *cylindrical* symmetry for each cyclopentadienyl ring, the molecular configuration conforms to the tetragonal point group D_{2d}-$\bar{4}2m$ (Figure 2) within the limits of accuracy. The corresponding bond lengths and angles for the iron–sulfur framework are identical within 2σ of the individual values. The close distributions of the chemically equivalent molecular parameters about their weighted averages (given in Tables III and IV) support the estimates of the standard deviations computed from the variance–covariance matrix. Hence, the "best values" of the molecular parameters utilized in this discussion are based on D_{2d} molecular symmetry. One of the two symmetry-related molecular twofold axes is crystallographically required.

The stereochemical consequence of only two Fe–Fe bonds in the molecule is a symmetrical deformation of the metal–sulfur cluster from a cubic T_d-$\bar{4}3m$ configura-

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(17) J. F. Blount, "A Three-Dimensional Crystallographic Fourier Summation Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix), University of Wisconsin, 1965.

(18) P. W. Sutton, "A Block-Diagonal Least-Squares Program for the CDC 1604," University of Wisconsin, 1962.

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(20) L. H. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 293 (1957).

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(22) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

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(24) D. L. Smith, "A Least-Squares Plane Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, 1962.

TABLE II

OBSERVED AND CALCULATED STRUCTURE FACTORS

H	K	L	FO	FC
4	0	0	260.2	-233.8
4	8	0	30.9	39.4
5	1	0	77.2	-85.3
5	3	0	59.0	-56.3
-5	3	0	56.1	-56.3
5	5	0	58.1	57.1
6	0	0	297.4	-250.3
6	8	0	57.5	66.3
7	1	0	158.5	-159.7
7	3	0	167.0	-174.0
-7	3	0	172.9	-174.0
7	5	0	79.4	86.1
8	0	0	319.8	-277.7
8	2	0	67.2	-67.8
8	8	0	46.8	41.4
9	1	0	132.4	-136.2
9	3	0	73.8	-81.3
-9	3	0	85.5	-81.3
10	2	0	101.6	-103.7
11	5	0	78.1	-70.1
12	0	0	72.4	68.2
13	1	0	64.1	65.4
13	5	0	60.6	-54.8
14	2	0	40.8	43.3
15	1	0	80.7	79.5
16	2	0	90.3	94.1
17	1	0	57.8	59.0
1	7	1	64.2	87.8
4	4	1	91.4	-101.6
-4	6	1	42.1	44.8
5	1	1	124.8	-136.8
5	3	1	44.1	-45.3
-5	5	1	38.0	-39.8
-6	2	1	61.8	-53.3
6	4	1	187.2	-192.6
-6	4	1	163.2	-163.6
7	1	1	214.7	-220.5
-7	1	1	147.4	-134.6
7	3	1	70.9	-74.2
-7	3	1	65.5	-72.9
-7	5	1	79.7	-80.3
7	7	1	93.6	-76.7
-7	7	1	54.4	-49.0
-8	2	1	60.9	-61.9
8	4	1	128.0	-128.6
-8	4	1	145.9	-145.6
9	1	1	72.3	-81.3
-9	3	1	116.6	-111.8
-9	5	1	97.8	-103.8
-10	2	1	94.3	-105.3
10	6	1	59.4	-42.2
-10	6	1	85.2	-79.2
11	1	1	53.2	47.8
-11	1	1	59.5	59.1
-11	3	1	63.9	-70.1
12	4	1	52.2	57.7
-12	6	1	53.9	-46.2
13	1	1	51.2	65.7
14	2	1	47.7	59.2
14	4	1	61.3	57.2
-15	3	1	52.8	53.5
-15	5	1	61.6	58.0
-16	2	1	100.5	109.8
-17	3	1	54.1	65.8
-17	5	1	79.1	70.1
-18	2	1	64.0	73.2
1	7	2	47.0	-60.3
2	6	2	44.5	-47.1
3	5	2	53.3	-50.3
3	7	2	47.0	-45.7
-3	7	2	87.2	90.9
4	0	2	151.9	161.8
-4	0	2	97.5	-106.1
4	2	2	57.8	-50.7
-4	4	2	66.5	73.6
-4	6	2	35.6	42.5
4	8	2	49.9	-47.7
5	3	2	139.8	142.9
-5	3	2	33.3	35.3
5	5	2	86.3	-84.1
-5	7	2	77.9	68.1
6	0	2	314.9	292.8
-6	2	2	82.9	-64.3
-6	4	2	58.3	64.0
6	8	2	63.3	-60.8
-7	1	2	126.9	131.4
7	3	2	166.2	165.8
-7	3	2	101.0	104.7
7	5	2	87.1	-89.7
8	0	2	136.0	143.8
-8	0	2	154.1	148.9
-8	2	2	51.0	56.4
-8	4	2	52.8	60.0
8	6	2	62.3	56.7
-9	1	2	180.2	180.6
9	3	2	55.2	64.1
10	0	2	57.1	-63.0
-10	0	2	63.4	75.6
-10	2	2	241.2	214.7
10	6	2	59.6	50.5
-10	6	2	81.2	-86.7
-11	1	2	143.8	146.5
-11	3	2	56.1	-58.0
11	5	2	95.5	82.4
12	0	2	55.4	-61.6
12	2	2	39.2	36.5
-12	2	2	93.5	86.3
-12	6	2	62.3	-52.5
-15	1	2	73.1	-69.8
-16	2	2	85.8	-93.4
-17	1	2	98.6	-100.1
-18	2	2	81.2	-92.6
-19	1	2	69.6	-75.9
0	4	3	85.5	-100.1
0	6	3	40.2	49.3
1	1	3	153.1	-148.3
-1	1	3	119.7	-118.2
1	3	3	98.3	108.1
1	7	3	45.4	-48.0
-2	4	3	45.9	-48.5
2	8	3	51.9	-53.1
3	1	3	92.4	98.0
3	3	3	79.8	84.0
-3	3	3	119.6	-120.3
-3	5	3	40.9	-55.2
4	2	3	57.5	46.7
-4	2	3	86.8	-88.9
4	4	3	140.1	146.8
-4	4	3	46.5	-51.3
-4	6	3	48.2	-51.1
-4	8	3	39.0	31.3
5	1	3	213.7	205.6
-5	3	3	177.2	-167.8
-5	5	3	30.4	-40.8
-5	7	3	47.8	43.4
6	2	3	108.3	-116.9
-6	2	3	61.7	-60.8
6	4	3	108.9	113.6
-6	6	3	40.5	-37.6
-6	8	3	54.1	54.5
7	1	3	131.1	139.9
-7	1	3	74.6	63.6
7	3	3	50.2	-49.8
-7	3	3	43.2	-44.1
7	5	3	64.2	-66.7
7	7	3	67.3	52.2
8	2	3	159.8	-153.0
-8	2	3	45.7	54.1
-8	4	3	37.6	31.3
8	6	3	37.8	-42.8
-9	1	3	62.5	-62.1
9	3	3	57.4	-54.9
-9	3	3	109.0	119.5
9	5	3	54.6	-44.9
-9	5	3	108.9	108.8
10	2	3	41.2	-46.9
-10	2	3	199.7	189.6
-10	6	3	56.1	61.2
11	1	3	73.9	-74.8
-11	1	3	108.5	-107.6
-11	3	3	94.1	108.2
-11	5	3	93.9	92.5
-12	2	3	126.7	126.4
12	4	3	61.6	-53.8
-12	6	3	60.4	52.3
13	1	3	60.4	-67.0
14	2	3	61.6	63.7
-16	2	3	63.9	-70.9
-17	3	3	46.6	-59.9
-18	2	3	80.6	-83.3
0	2	4	91.9	-92.4
0	4	4	53.5	56.9
0	6	4	46.6	55.2
-1	1	4	108.7	-107.8
1	3	4	65.7	67.5
1	7	4	98.1	86.7
-1	7	4	54.2	43.2
2	0	4	44.7	42.0
-2	0	4	193.0	-191.8
2	2	4	58.8	-61.5
2	4	4	54.9	61.0
2	6	4	35.0	29.5
-3	1	4	51.7	48.0
3	3	4	32.1	-35.3
-3	3	4	76.2	-76.5
3	7	4	77.4	63.9
4	0	4	65.8	-64.3
-4	0	4	93.3	-91.6
4	2	4	52.1	57.7
-4	2	4	50.0	44.4
4	4	4	57.1	59.5
-4	4	4	49.2	-42.7
-4	6	4	72.8	-74.4
5	1	4	87.9	96.2
-5	1	4	36.8	47.3
5	3	4	79.9	-81.2
-5	3	4	91.7	-93.4
5	5	4	79.4	77.2
-5	7	4	71.7	-60.3
6	0	4	94.0	-98.7
6	2	4	146.1	154.0
-6	2	4	98.5	98.2
-6	4	4	51.5	-45.7
6	6	4	64.7	-60.9
-6	6	4	60.5	-60.7
7	1	4	190.3	189.4
7	3	4	45.2	-42.5
-7	3	4	83.2	-83.6
-7	7	4	49.2	-63.0
-8	0	4	64.4	65.8
8	2	4	99.4	107.5
-8	4	4	47.0	-48.5
8	6	4	76.8	-72.6
9	1	4	47.1	49.3
-9	3	4	119.3	103.8
-9	5	4	54.5	-69.0
10	0	4	58.6	59.0
-10	0	4	139.2	143.3
-10	2	4	137.2	-122.3
-10	6	4	63.5	57.1
-11	1	4	100.9	-108.2
-11	3	4	135.9	124.3
-11	5	4	50.7	-50.5
12	2	4	77.6	-86.7
-12	2	4	68.7	-81.8
-12	6	4	86.8	81.3
13	1	4	71.1	-73.2
-13	1	4	100.2	-101.9
-13	3	4	45.0	44.8
14	2	4	93.7	-93.8
-14	6	4	50.9	41.8
15	1	4	71.0	-65.1
-18	2	4	52.9	54.9
0	2	5	99.1	-93.7
0	6	5	78.2	-71.6
0	8	5	38.2	29.7
1	3	5	190.4	-187.9
-1	3	5	123.7	-120.3
2	2	5	75.0	-71.8
-2	2	5	33.3	-27.0
-2	4	5	165.0	-156.0
2	6	5	36.5	-44.0
-2	6	5	61.2	-63.8
2	8	5	47.9	45.9
-3	1	5	131.7	-127.3
-3	3	5	49.3	-50.7
-3	7	5	58.6	-52.6
4	2	5	88.2	82.0
-4	2	5	66.4	61.0
-4	4	5	158.0	-155.5
-5	1	5	134.7	-134.7
5	3	5	179.8	178.5
-5	3	5	48.0	46.4
5	5	5	111.1	118.1
-5	7	5	76.7	-60.3
6	2	5	201.3	188.7
-6	2	5	164.5	152.1
6	6	5	83.7	90.8
-6	6	5	47.0	46.2
-7	1	5	64.8	-56.3
7	3	5	108.0	112.3
-7	3	5	105.1	104.6
7	5	5	78.5	76.8
-7	5	5	45.5	41.7
-7	7	5	51.3	-39.7
8	2	5	81.4	83.1
-8	2	5	41.5	77.2
-8	4	5	98.3	92.1
8	6	5	65.0	58.3
-9	1	5	119.8	125.8
-9	3	5	43.4	43.2
-10	2	5	92.1	-77.3
-10	4	5	141.6	135.9
-11	1	5	143.4	145.0
-11	7	5	89.3	61.5
12	2	5	97.3	-104.4
-12	2	5	100.3	-93.1
13	3	5	69.0	-70.0
13	5	5	69.3	-66.7
14	2	5	97.1	-100.0
-14	2	5	60.6	-67.2
0	0	6	71.8	71.5
0	2	6	156.4	146.0
0	6	6	48.5	-50.4
1	1	6	55.3	47.2
-1	1	6	169.2	156.7
-1	3	6	67.3	67.7
1	7	6	73.4	-53.6
-1	7	6	72.7	-63.9
2	0	6	22.7	-87.0
-2	0	6	271.1	264.6
2	2	6	62.4	59.4
-2	2	6	88.8	84.5
-2	8	6	41.8	-39.4
3	1	6	62.9	-55.7
-3	1	6	106.1	105.5
3	3	6	81.7	-82.1
-3	3	6	185.3	177.2
-3	5	6	46.2	-52.0
-3	7	6	56.5	-43.3
4	0	6	171.9	-176.4
-4	0	6	381.8	345.3
4	2	6	115.7	-120.3
-4	6	6	66.9	66.0
-4	8	6	56.0	-52.2
5	1	6	157.1	-157.2
-5	1	6	45.7	-50.3
5	3	6	53.9	-40.5
-5	3	6	171.7	160.7
-5	5	6	47.6	-45.0
5	7	6	67.0	53.7
6	0	6	42.6	-43.1
-6	0	6	145.0	135.8
6	2	6	160.4	-158.1
-6	2	6	95.2	-107.7
6	6	6	61.3	53.9
-6	6	6	85.9	78.6
7	1	6	132.9	-126.0
-7	1	6	78.8	-76.2
-7	3	6	80.0	79.9
-8	0	6	67.7	-67.6
8	2	6	54.2	-58.0
-8	2	6	31.8	-42.5
-8	6	6	43.5	31.2
-9	1	6	58.2	-59.6
-9	3	6	80.9	-75.9
-9	5	6	55.4	50.3
-10	0	6	221.8	-216.7
-10	8	6	70.7	53.5
11	1	6	78.1	75.2
-11	1	6	45.8	-64.3
-11	3	6	128.3	-125.1
-11	5	6	52.4	57.0
-12	0	6	149.9	-157.4
12	2	6	93.5	94.5
13	1	6	93.6	93.6
-13	3	6	63.7	-61.0
14	2	6	71.1	78.7
-16	0	6	67.4	77.2
0	2	7	80.9	86.7
0	6	7	57.2	52.2
1	1	7	74.8	-77.0
-1	3	7	84.6	77.9
-1	5	7	48.0	39.3
2	2	7	40.0	-32.0
-2	2	7	80.0	77.1
2	4	7	159.5	-153.0
-2	4	7	147.3	142.5
-2	6	7	80.4	76.8
3	1	7	151.9	-150.4
-3	1	7	173.4	163.3
3	3	7	73.6	-69.2
-3	3	7	76.8	74.9
-3	5	7	43.6	28.8
3	7	7	74.4	-46.3
-3	7	7	81.9	71.4
4	2	7	42.6	-42.7
-4	2	7	35.1	-39.6
4	4	7	109.7	-110.7
-4	4	7	227.8	219.8
4	6	7	48.1	-42.5
-5	1	7	227.9	218.1
5	3	7	94.9	-94.4
-5	3	7	87.6	86.5
-5	7	7	103.2	76.1
-6	2	7	91.5	-86.0
-6	4	7	148.7	126.9
6	6	7	74.8	-70.0
-7	1	7	76.3	78.5
7	3	7	60.1	-65.7
-8	2	7	74.9	-72.8
-9	1	7	92.1	-84.6
-9	3	7	68.8	-61.0
-9	5	7	78.1	-74.2
10	2	7	49.5	45.5
-10	4	7	149.8	-128.1
-11	1	7	106.4	-95.2
11	3	7	56.3	56.0
-11	3	7	61.5	-56.9
-11	5	7	56.9	-55.5
-11	7	7	73.5	-47.2
12	2	7	70.7	73.9
-12	4	7	108.8	-106.5
-16	4	7	64.1	66.4
-17	1	7	68.5	56.0
-18	4	7	78.4	66.6
-20	2	7	49.7	47.0
0	0	8	108.0	112.2
0	2	8	54.7	-60.0
0	8	8	53.0	-34.7
-1	1	8	62.0	-66.5
1	3	8	102.9	101.2
1	5	8	82.4	-79.1
-1	5	8	51.8	-46.6
2	0	8	219.8	205.3
-2	0	8	102.2	-99.3
-2	2	8	72.9	-69.5
2	8	8	59.9	-51.0
-3	1	8	102.3	-99.5
3	3	8	114.6	118.5
-3	3	8	147.6	-145.3
3	5	8	75.6	-75.0
-3	5	8	62.8	66.4
4	0	8	155.3	168.4
-4	0	8	396.1	-361.2
-4	2	8	42.8	-40.9
-4	8	8	57.8	64.3
5	1	8	58.4	61.4
-5	1	8	86.2	-80.7
-5	3	8	176.3	-153.7
-5	5	8	103.6	103.7
-6	0	8	258.0	-242.6
6	2	8	53.8	58.5
-6	8	8	49.6	45.7
-7	3	8	75.1	-67.8
7	5	8	73.9	66.7
-8	0	8	41.6	40.8
-8	2	8	54.7	55.0
9	1	8	48.9	-45.4
-9	1	8	78.2	82.0
-9	3	8	52.1	54.2
-10	0	8	155.2	146.0
-10	4	8	41.7	34.7
-10	8	8	47.5	-45.0
-11	1	8	110.7	112.5
-11	3	8	78.7	81.7
-11	5	8	48.3	-40.7
-12	0	8	132.1	133.8
-12	2	8	47.1	45.2
-13	1	8	93.1	91.3
-14	2	8	62.8	64.5
-16	0	8	87.9	-88.8
-16	2	8	44.2	20.3
-18	0	8	73.6	-83.5
-19	1	8	69.7	-65.7
-20	2	8	50.1	-57.1
0	4	9	106.8	85.8
1	1	9	136.3	135.8
-1	1	9	79.5	81.5
2	4	9	117.3	117.4
3	1	9	102.1	107.8
-3	1	9	87.6	-92.4
4	2	9	44.1	-41.9
4	4	9	72.2	69.6
-4	4	9	107.1	-107.7
-5	1	9	149.9	-144.4
-5	3	9	41.8	-40.3
-5	7	9	70.5	-55.9
-6	4	9	106.7	-101.1
7	1	9	58.3	-57.1
-7	1	9	60.9	-59.5
-7	3	9	65.9	-69.9
8	4	9	76.4	-61.5
-9	1	9	41.8	47.2
-10	4	9	76.2	77.2
-11	1	9	66.7	64.7
-11	5	9	49.9	52.8
-12	2	9	59.6	60.7
-12	4	9	91.6	78.9
-13	5	9	69.1	58.6
-14	2	9	63.0	64.2
-15	1	9	56.0	-47.0
-16	2	9	44.9	52.5
-18	4	9	61.5	-49.8
-20	2	9	56.5	-52.4
0	0	10	107.6	-109.0
0	2	10	43.0	45.0
1	3	10	65.6	-73.0
-1	3	10	51.4	-63.2
1	5	10	67.9	61.7
-1	5	10	71.2	60.8
2	0	10	100.5	-118.1
-2	0	10	47.4	-35.4
2	2	10	45.6	46.3
-2	4	10	48.5	46.0
3	1	10	58.4	57.3
-3	3	10	49.5	50.4
-4	0	10	63.1	71.9
4	2	10	41.6	48.8
-4	2	10	37.2	-55.0
-5	3	10	46.9	52.1
-5	5	10	61.1	-62.2
6	0	10	79.6	97.2
-6	0	10	63.6	60.1
-7	1	10	71.0	67.7
7	5	10	65.9	-61.6
8	0	10	67.9	74.8
-11	3	10	57.0	-68.3
-13	1	10	76.7	-66.4
-14	2	10	83.3	-77.9
-14	6	10	56.0	50.4
-15	1	10	76.3	-66.8
-15	3	10	56.1	62.5
-16	2	10	59.8	-51.0
-18	0	10	58.0	62.3
-20	2	10	51.2	37.8
0	4	11	76.5	-68.7
1	1	11	67.8	-68.7
-1	1	11	77.0	-80.8
2	2	11	69.9	72.4
3	3	11	50.0	54.5
-3	3	11	60.8	-58.2
4	2	11	50.1	57.0
-4	2	11	39.3	-45.8
-4	6	11	53.7	-53.4
6	4	11	62.7	65.6
7	1	11	63.8	67.0
-8	2	11	74.5	75.8
8	4	11	65.9	51.8
-9	3	11	47.4	61.7
-10	2	11	73.2	78.8
-11	3	11	49.9	46.9
-14	2	11	67.7	-67.5
-15	1	11	58.7	54.2
-16	2	11	63.6	-60.8
0	2	12	51.9	-64.5
1	1	12	63.7	-60.9
-1	5	12	65.8	-18.9
2	2	12	67.6	-69.9
3	1	12	93.2	-89.9
-3	1	12	53.4	54.2
4	0	12	55.0	-51.6
4	2	12	52.6	-55.9
-4	2	12	90.5	99.9
6	0	12	77.0	-80.9
-6	0	12	88.6	78.9
-7	3	12	69.9	66.1
-8	0	12	81.6	76.9
8	2	12	70.7	57.8
-8	6	12	54.1	42.8
-9	3	12	65.4	59.1
-10	2	12	56.1	-70.1
-10	6	12	70.7	56.7
-11	1	12	59.2	-62.1
-11	3	12	45.5	43.0
-12	2	12	44.3	-43.1
-14	0	12	70.4	-64.4
-15	3	12	59.1	-56.3
1	3	13	69.5	-74.3
2	2	13	53.2	-62.1
2	4	13	52.7	-33.1
3	3	13	56.1	-63.2
-3	3	13	77.1	76.8
-4	2	13	74.3	79.4
-4	6	13	59.5	54.2
-5	3	13	84.7	68.5
-6	4	13	64.1	55.2
-6	6	13	59.4	39.0
-7	1	13	64.0	60.8
-7	3	13	50.9	36.3
8	2	13	63.3	50.0
-8	4	13	75.9	66.9
-9	1	13	63.5	66.1
-10	2	13	81.7	-82.8
-11	3	13	61.4	-58.8
-12	2	13	76.4	-69.7
-13	3	13	48.7	-37.7
-14	4	13	61.3	-59.3
0	0	14	75.0	64.6
0	2	14	47.3	48.0
2	2	14	55.7	54.2
-4	2	14	88.9	-88.5
-5	1	14	76.1	-74.4
-6	0	14	77.5	-82.7
-6	2	14	45.7	-53.3
-7	1	14	58.7	-56.3
-7	3	14	72.4	-65.0
-8	0	14	77.9	-77.0
-9	3	14	71.2	-67.2
-10	0	14	68.5	-82.5
-11	1	14	60.4	52.2
-12	2	14	47.6	46.0
-14	0	14	75.0	82.0
-16	0	14	59.1	60.3
-3	1	15	73.4	67.6
-6	2	15	47.8	-40.0
-8	4	15	65.5	-58.4
-9	1	15	61.8	-66.1
-14	4	15	64.1	49.6
-2	0	16	53.0	-65.9
-8	0	16	59.8	64.3
-10	0	16	52.5	64.0

tion of *regular* interpenetrating concentric tetrahedra (based on *six* equivalent metal–metal bonds)[25] to one of reduced D_{2d} symmetry. The following geometric features are inherent in the Fe_4S_4 framework: (1) Two Fe–Fe bonds of length 2.650 ± 0.006 A *vs.* four nonbonding Fe···Fe distances of average value 3.365 ± 0.006 A and two larger nonbonding S···S distances of 3.334 ± 0.009 A *vs.* four smaller nonbonding S···S distances of average value 2.880 ± 0.007 A for the distorted tetrahedron of sulfur atoms. The resulting dihedral angle of the two Fe_2S_2 fragments at the bonding Fe–Fe edges is 142.3 ± 0.4° compared to the average dihedral angle of 161.0° (individual esd, 0.5°) for the other four Fe_2S_2 fragments along the nonbonding Fe···Fe edges. (2) A shorter mean Fe–S bond length of 2.204 ± 0.004 A for these two identical Fe_2S_2 fragments containing the Fe–Fe bonds compared to the mean bond length of 2.250 ± 0.008 A for the four Fe–S bonds linking the two Fe_2S_2 fragments to each other. These Fe–S bond lengths compare favorably with the mean lengths for the chemically equivalent Fe–S bonds found

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(25) The probable existence of a $[C_5H_5CrS]_4$ tetramer with this symmetrical configuration of holohedral tetrahedral symmetry (T_d) such that each chromium atom obtains a closed-shell electronic configuration is in accord with the announcement by Professor E. O. Fischer (München) at the Second International Symposium on Organometallic Chemistry (Madison, Wis., Aug 30–Sept 3, 1965) that this compound has been prepared. Allusion to this cyclopentadienylchromium sulfide complex was first made by Fischer and co-workers (E. O. Fischer, K. Ulm, and H. P. Fritz, *Chem. Ber.*, **93**, 2167 (1960)) in their paper describing the preparation and characterization of the corresponding oxide complex $[C_5H_5CrO]_4$. Presumably this latter molecular complex also possesses the T_d configuration.

TABLE III

MOLECULAR BOND LENGTHS (A) WITH STANDARD DEVIATIONS[a]

$Fe_1—Fe_2$	2.650 (6)	$Fe_1—C_5$	2.18 (2)
$Fe_1\cdots Fe_1'$	3.355 (16)	$—C_6$	2.12 (2)
$Fe_1\cdots Fe_2'$	3.362 (9)	$—C_7$	2.09 (3)
$Fe_2\cdots Fe_2'$	3.372 (9)	$—C_8$	2.12 (2)
		$—C_9$	2.15 (3)
	3.365 (6) (wtd av)	$Fe_2—C_{10}$	2.12 (2)
$S_3\cdots S_4$	3.334 (9)	$—C_{11}$	2.10 (2)
		$—C_{12}$	2.20 (2)
$S_3\cdots S_3'$	2.883 (14)	$—C_{13}$	2.20 (2)
$S_3\cdots S_4'$	2.874 (10)	$—C_{14}$	2.10 (3)
$S_4\cdots S_4'$	2.891 (16)		2.14 (1) (wtd av)
	2.880 (7) (wtd av)	$C_5—C_6$	1.49 (3)
$Fe_1—S_3$	2.201 (9)	$C_6—C_7$	1.42 (3)
$Fe_1—S_4$	2.202 (8)	$C_7—C_8$	1.47 (3)
$Fe_2—S_3$	2.198 (8)	$C_8—C_9$	1.40 (3)
$Fe_2—S_4$	2.215 (9)	$C_9—C_5$	1.48 (3)
	2.204 (4) (wtd av)	$C_{10}—C_{11}$	1.45 (3)
		$C_{11}—C_{12}$	1.43 (3)
$Fe_1—S_3'$	2.248 (10)	$C_{12}—C_{13}$	1.44 (3)
$Fe_2—S_4'$	2.252 (11)	$C_{13}—C_{14}$	1.41 (3)
		$C_{14}—C_{10}$	1.48 (3)
	2.250 (8) (wtd av)		1.45 (1) (wtd av)

[a] Standard deviations of last significant figures are given in parentheses.

TABLE IV

BOND ANGLES (DEG) WITH STANDARD DEVIATIONS[a]

$S_3–Fe_1–S_4$	98.4 (3)	$Fe_1–S_3–S_4'$	93.5 (3)
$S_3–Fe_2–S_4$	98.1 (2)	$Fe_1–S_4–S_4'$	93.1 (2)
		$Fe_2–S_3–S_3'$	93.5 (2)
	98.2 (2) (wtd av)	$Fe_2–S_4–S_5'$	93.3 (3)
$S_3–Fe_1–S_3'$	80.8 (4)		
$S_3–Fe_2–S_4'$	80.5 (3)		93.3 (2) (wtd av)
$S_4–Fe_1–S_3'$	80.5 (2)	$S_3–S_3'–S_4$	70.8 (2)
$S_4–Fe_2–S_4'$	80.6 (3)	$S_4–S_4'–S_3$	70.7 (3)
	80.6 (2) (wtd av)		70.8 (2) (wtd av)
$S_3'–Fe_1–Fe_2$	98.8 (3)	$C_5–C_6–C_7$	109.4 (2.1)
$S_4'–Fe_2–Fe_1$	98.6 (3)	$C_6–C_7–C_8$	107.8 (2.3)
		$C_7–C_8–C_9$	108.3 (2.1)
	98.7 (2) (wtd av)	$C_8–C_9–C_5$	110.4 (2.2)
		$C_9–C_5–C_6$	104.1 (2.0)
$S_3–Fe_1–Fe_2$	52.9 (2)	$C_{10}–C_{11}–C_{12}$	108.9 (2.1)
$S_4–Fe_1–Fe_2$	53.4 (2)	$C_{11}–C_{12}–C_{13}$	110.0 (2.1)
$S_3–Fe_2–Fe_1$	53.0 (2)	$C_{12}–C_{13}–C_{14}$	105.3 (2.0)
$S_4–Fe_2–Fe_1$	52.9 (2)	$C_{13}–C_{14}–C_{10}$	112.3 (2.1)
		$C_{14}–C_{10}–C_{11}$	103.3 (2.1)
	53.0 (1) (wtd av)		
			108.0 (8) (wtd av)
$Fe_1–S_3–Fe_2$	74.1 (2)		
$Fe_1–S_4–Fe_2$	73.7 (2)		
	73.9 (2) (wtd av)		
$Fe_1–S_3–Fe_1'$	97.9 (4)		
$Fe_1–S_4–Fe_2'$	98.0 (3)		
$Fe_2–S_3–Fe_1'$	98.2 (3)		
$Fe_2–S_4–Fe_2'$	98.0 (3)		
	98.0 (2) (wtd av)		

[a] Standard deviations of last significant figures are given in parentheses.

TABLE V

EQUATION OF MOLECULAR PLANE AND DISTANCES (A) OF ATOMS FROM THESE PLANES[a]

(a) Plane through Fe_1, Fe_2, and Midpoint of $Fe_1'–Fe_2'$

$$0.318X - 0.708Y - 0.631Z + 1.345 = 0$$

S_3'	0.002	C_9	0.30	C_{12}	−0.29
S_4'	−0.006	C_5	1.26	C_{11}	1.02
S_3	−1.662	C_8	−1.01	C_{13}	−1.28
S_4	1.672	C_6	0.40	C_{10}	0.91
		C_7	−0.96	C_{14}	−0.55

(b) Plane through Fe_1', Fe_2' and Midpoint of $Fe_1–Fe_2$

$$0.318X + 0.708Y - 0.631Z - 2.047 = 0$$

S_3	−0.002	C_9	1.75	C_{12}	−1.75
S_4	0.006	C_8	2.06	C_{13}	−2.46
S_3'	1.662	C_7	3.07	C_{14}	−3.29
S_4'	−1.672	C_6	3.37	C_{10}	−3.13
		C_5	2.54	C_{11}	−2.09

(c) Plane through C_5, C_6, C_7, C_8, and C_9

$$-0.398X + 0.532Y - 0.748Z + 0.977 = 0$$

C_5	−0.00	C_7	−0.00	C_9	0.00
C_6	0.00	C_8	0.00	Fe_1	−1.74

(d) Plane through C_{10}, C_{11}, C_{12}, C_{13}, and C_{14}

$$0.842X + 0.524Y - 0.130Z - 3.987 = 0$$

C_{10}	−0.02	C_{12}	−0.20	C_{14}	0.01
C_{11}	0.03	C_{13}	0.01	Fe_2	1.75

(e) Plane through S_3, S_3', and S_4

$$-0.407X + 0.500Y - 0.764Z + 4.259 = 0$$

C_5	3.11	Fe_1	1.33
C_6	3.07	Fe_2	−0.53
C_7	3.03	S_4'	−2.35
C_8	3.06	Fe_1'	−1.57
C_9	3.11	Fe_2'	−1.58

(f) Plane through S_3, S_4, and S_4'

$$0.858X + 0.499Y - 0.121Z - 7.186 = 0$$

C_{10}	−3.08	Fe_2	−1.34
C_{11}	−3.07	Fe_1	0.53
C_{12}	−3.16	S_3'	2.35
C_{13}	−3.11	Fe_1'	1.58
C_{14}	−3.07	Fe_2'	1.58

[a] The equation of each plane is expressed in orthogonal coordinates X, Y, and Z, which are related to the monoclinic cell coordinates by the transformation $X = ax + cz \cos\beta$, $Y = by$, and $Z = cz \sin\beta$.

in $[C_2H_5SFe(CO)_3]_2$ (2.26 A),[26] $[C_2H_5SFe(NO)_2]_2$ (2.27 A),[27] $CsFe_4S_3(NO)_7 \cdot H_2O$ (2.25 and 2.20 A),[28] $[SFe(CO)_3]_2$ (2.23 A),[10] and $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ (2.23 and 2.22 A).[11] (3) A larger average S–Fe–S angle of 98.2 ± 0.2° and a smaller average Fe–S–Fe angle of 73.9 ± 0.2° for the two identical Fe_2S_2 fragments compared to the average value of 80.6 ± 0.3° for the other S–Fe–S angles and the average value of 98.0 ± 0.2° for the other Fe–S–Fe angles. Hence, the Fe–Fe bonds in the two identical Fe_2S_2 fragments are responsible for the resulting molecular geometry with the sharp Fe–S–Fe bridge angles of 74° (av). Similar remarkably acute Fe–S–Fe angles for the symmetrical electron-pair bridge bonds in $[C_2H_5SFe(CO)_3]_2$ (68° (av)),[26] $[C_2H_5SFe(NO)_2]_2$ (74°),[27] $CsFe_4S_3(NO)_7 \cdot H_2O$ (75° (av)),[28] $[SFe(CO)_3]_2$ (70° (av)),[10] $[S_2Fe_3(CO)_9][S_2Fe_2(CO)_6]$ (71° (av) and 70°)[11] also are the result of strong Fe–Fe bonds which in these complexes vary in average length from 2.55 to 2.72 A.

The equivalence both the carbon–carbon bond lengths in the cyclopentadienyl rings and of the (cyclopentadienyl carbon)–iron distances within their standard deviations (Table III) is consistent with a uniform delocalized bonding of each ring with its iron atom. The least-squares plane through each of the cyclopentadienyl rings (Table V, (c) and (d)) show that the ring atoms do not deviate significantly from coplanarity. No evidence of unusual cyclopentadienyl ring libration

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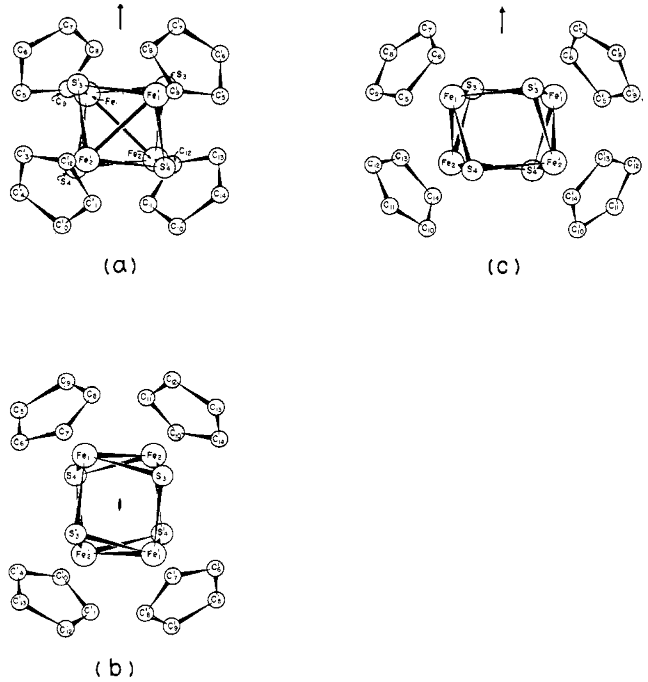

Figure 2.—Projections of the molecule down the three orthogonal symmetry directions corresponding to the tetragonal point group D_{d2} (based on cylindrical symmetry for the cyclopentadienyl rings). The direction of the *crystallographic* twofold axis is indicated for each of the three views. (a) Projection down the principal molecular S_4-$\bar{4}$ axis which contains two vertical σ_d mirror planes at right angles to each other. (b) Projection down one of the two symmetry-related molecular C_2-2 axes. (c) Projection down the other symmetry-related molecular C_2-2 axis which is crystallographically required.

is indicated from the three-dimensional Fourier and electron-density difference maps or from the isotropic atomic thermal parameters listed in Table I. The perpendicular distances from the iron atoms to the mean plane of their cyclopentadienyl carbon rings (Table V, (c) and (d)) are 1.74, and 1.75 A; the average value of 1.75 A is similar to the corresponding perpendicular Fe–(cyclopentadienyl ring) distance in $[C_5H_5Fe(CO)_2]_2$ (1.74 A),[29] $(C_6H_5C_2CO_2CH_3)_3COFe(CO)_2$ (1.71 A),[30] and $[C_5H_4CH_2Fe(CO)_4]Fe(CO)_2$ (1.67 A),[31] but appears significantly longer than the corresponding perpendicular distance in ferrocene (1.66 A),[32] dibenzoylferrocene (1.66 A),[33] α-keto-1,1′-trimethyleneferrocene (1.64 A),[34] and 1,1′-tetramethyleneferrocene (1.64 A).[35] These differences may be interpreted in terms of a weaker (cyclopentadienyl ring)–iron interaction for complexes with only one cyclopentadienyl ring coordinated to an iron compared to that for complexes with two cyclopentadienyl rings bonded to an iron.

The packing of the four molecules in the unit cell as viewed along the *b* axis is shown in Figure 3. The shortest intermolecular C···C distances of 3.6 A and C···S distances of 3.8 A do not indicate any abnormal CH···HC and CH···S interactions other than the usual van der Waals forces.

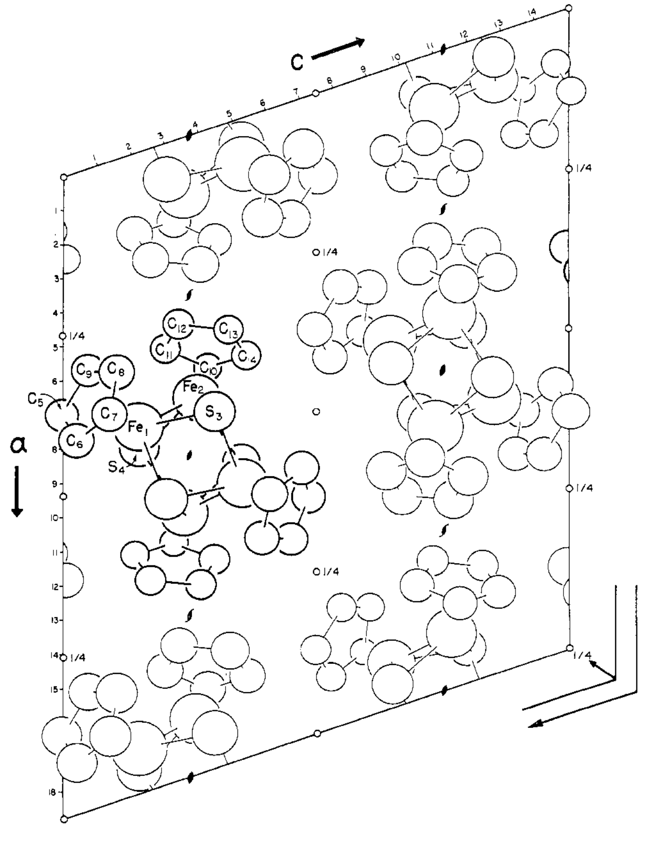

Figure 3.—Molecular packing in the unit cell viewed down the [010] direction.

The coordination about each of the two crystallographically independent iron atoms projected down a line perpendicular to its cyclopentadienyl ring is given in Figure 4. It is noteworthy that for each iron atom the ring of cyclopentadienyl carbon atoms is parallel within 2° ± 10′ to the plane through the three sulfur ligands (Table V, (e) and (f)). The localized environment of the one cyclopentadienyl ring, one iron, and three sulfur ligands about each iron atom is not unlike that observed for each metal atom in $[C_5H_5Mo(CO_3)]_2$,[36] $C_5H_5Nb(CO)_4$,[37] and $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$.[38] However, a symmetrical distortion in $[C_5H_5FeS]_4$ due to the coordination of the iron ligand to two of the three sulfur ligands results in two sets of ligand–metal–ligand angles of 80.6° (av) and 53.1° (av) (see Figure 4) rather than the corresponding angles of approximately 76° found for the four nonbonding ligands in each of the above-mentioned complexes. With the assumption that the cyclopentadienyl groups occupy three coordination sites, the bonding of these complexes has been interpreted in terms of a seven-coordinated metal.[37,38] The three normally σ-type metal orbitals directed toward the metal-coordinated cyclopentadienyl ring can be *delocalized* under assumed C_{3v} local symmetry into one

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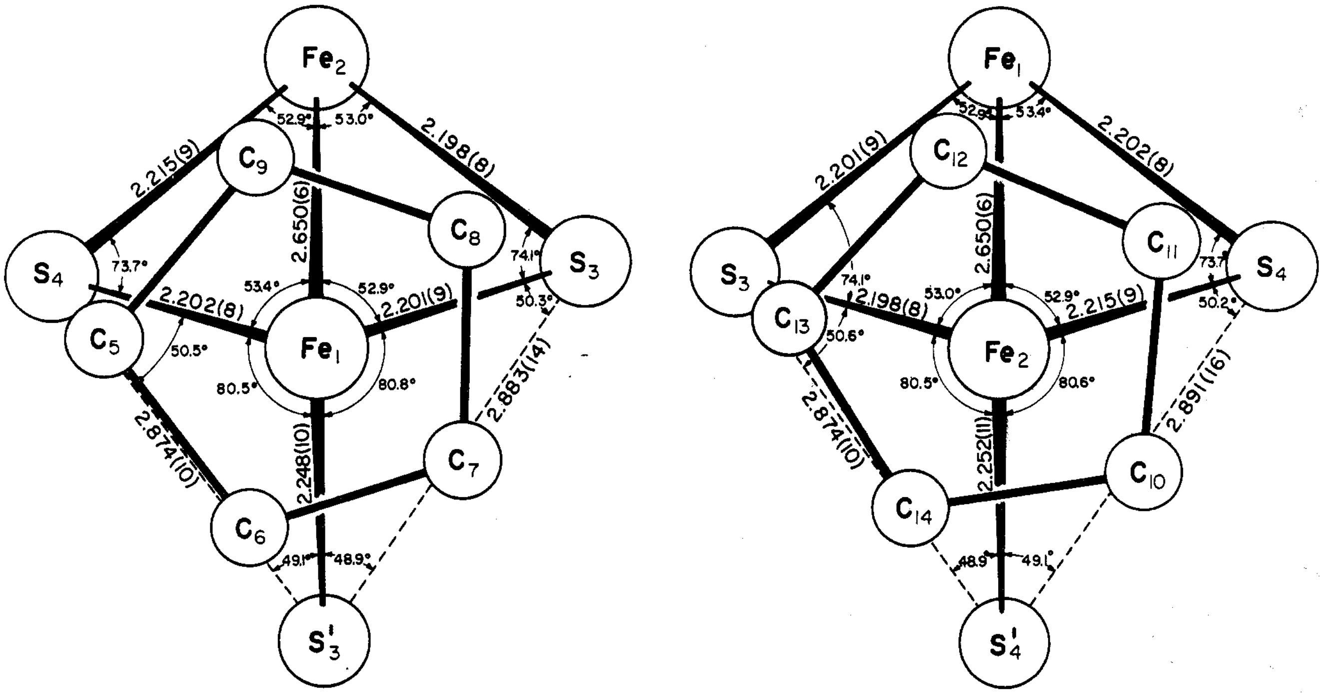

Figure 4.—Localized environment about each of the two crystallographically independent iron atoms of $[C_5H_5FeS]_4$ projected along the normal of the cyclopentadienyl ring. The essentially identical orientation of the cyclopentadienyl ring relative to the other iron and three sulfur ligands is shown for both Fe_1 and Fe_2. The close conformity of the molecular parameters for the iron–sulfur framework to the vertical σ_d mirror plane is seen.

orbital of a_1 symmetry and one pair of e symmetry which interact by direct overlap with the appropriate orbitals of equivalent symmetry belonging to the cyclopentadienyl ring. Under this simplified perfect-pairing bonding description the resulting *bonding* MO's contain the three pairs of electrons.

Since submission of our paper, we have received a preprint from Drs. R. A. Schunn, C. J. Fritchie, Jr., and C. T. Prewitt [*Inorg. Chem.*, **5**, 892 (1966)] on the crystal structure of another crystal modification of $[C_5H_5FeS]_4$. We are indebted to them for making their results available to us prior to publication in order to allow a detailed comparison of their structure of the orthorhombic phase with our structure of the monoclinic phase. Schunn, Fritchie, and Prewitt isolated and characterized by X-ray diffraction both the monoclinic and orthorhombic phases of $[C_5H_5FeS]_4$, but they carried out a complete structural analysis of only the orthorhombic phase. We isolated and characterized by a complete structure determination only the monoclinic phase. A comparison of their monoclinic crystal data with ours shows all three corresponding lattice lengths and the β angle to agree very well within 0.5 of our estimated uncertainties.

A comparison of the two sets of molecular parameters is informative. Although the molecular packing is different for the two phases, the corresponding bond lengths are amazingly similar, as can be seen from the tabulation of the "best values" of these parameters based on D_{2d}-$\bar{4}2m$ symmetry in which each cyclopentadienyl ring is assumed to possess cylindrical symmetry (Table VI). In the monoclinic crystal modification one of the two symmetry-related molecular twofold axes is crystallographically required, while in the orthorhombic crystal form one of the two vertical σ_d mirror planes is crystallographically demanded. The significant deviation of the two cyclopentadienyl carbon atoms of the two crystallographically independent rings from an idealized vertical mirror plane in the monoclinic phase of $[C_5H_5FeS]_4$ is indicated in Figures 2 (a) and 4. In contrast, each molecule of the orthorhombic phase has two cyclopentadienyl rings bisected by a mirror plane of Pnam with the other two rings being mirror images of each other.

TABLE VI

BOND LENGTHS (A)

	Monoclinic phase	Orthorhombic phase
Fe–Fe	2.650 ± 0.006	2.618 ± 0.002 2.644 ± 0.002 } 2.631 (av)
Fe–S	2.204 ± 0.004 2.250 ± 0.008	2.206 ± 0.002 2.256 ± 0.003
Fe–C_5F_5 (ring center)	1.74 and 1.75	1.757 ± 0.005

The excellent agreement of the molecular parameters for the two phases indicates that "good" photographic data can yield under proper treatment significant structural results which compare favorably with the generally more precise results obtained from "good" counter data.

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