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CRYSTAL AND MOLECULAR STRUCTURE OF $(C_5H_5)_2Fe_2(CO)_3CS$, A CARBONYL, THIOCARBONYL-BRIDGED DIIRON COMPLEX

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Summary

The crystal and molecular structure of $(Cp)_2Fe_2(CO)_3CS$, dicarbonyldi-η-cyclopentadienyl-μ-carbonyl-μ-thiocarbonyldiiron, has been determined by single crystal X-ray techniques. It crystallizes in space group $P2_1/c$ with a 14.508(8) Å, b 13.618(5) Å, c 15.193(7) Å, β 110.50(6)° and eight molecules per cell (two per asymmetric unit). A modified Patterson superposition technique yielded the initial model which refined to a residual index of $R = 0.070$ using 3643 observed reflections ($|F_0| > 3\sigma|F_0|$). The thiocarbonyl group occupies one of the two bridging positions with concomitant lengthening of the C=S distance to 1.60(1) Å. The Fe—Fe distance is 2.505(2) Å, intermediate between that found for related complexes with two carbonyl bridges, 2.531 Å, and two thiocarbonyl bridges, 2.482 Å. The cyclopentadienyl groups are *cis* to one another in the complex.

Introduction

To date only a few complexes containing thiocarbonyl bridges have been reported [1—5], all demonstrating the preference of the CS group for a bridging over a terminal position. We decided to undertake an X-ray crystal structure analysis of the dicarbonyldi-η-cyclopentadienyl-μ-carbonyl-μ-thiocarbonyldiiron, $Cp_2Fe_2(CO)_3CS$, complex, which contains both a thiocarbonyl and carbonyl bridge in the same molecule, to determine its structural characteristics and any differences and/or similarities to the carbonyl [6] and thiocarbonyl [1] analogs. Of particular interest are the deviations, if any, in the iron—iron and iron—bridging carbon distances when the number of bridging thiocarbonyls is changed. The increasing number of structurally characterized metal—metal bonded dimers is an indication of the current interest in metal cluster compounds, with dimers being considered the simplest building blocks for larger clusters. The thiocarbonyl ligand described in this paper is a unique new bridging ligand that may lead to many novel clusters.

Experimental

Crystal data

$Cp_2Fe_2(CO)_3CS$, M.W. = 369.99, monoclinic $P2_1/c$, a 14.508(8), b 13.618(5), c 15.193(7) Å, β 110.50(6)°, V 2811.56 Å^3, ρ_c 1.753 g cm^{-3}, $Z = 8$, μ 22.6 cm^{-1} for Mo-K_α.

Crystals of the title compound, whose preparation is discussed elsewhere [5], were obtained from Quick and Angelici. A rectangular prismatic crystal of approximate dimensions 0.4 mm × 0.3 mm × 0.2 mm was selected, mounted on a glass fiber with Elmer's Glue-All and attached to a standard goniometer head. Four preliminary ω-oscillation photographs, taken at various χ and ϕ settings on a four-circle diffractometer, provided the coordinates of ten independent reflections which were input into an automatic indexing program [7]. The resulting reduced cell and reduced cell scalars indicated $2/m$ (monoclinic) symmetry. Observed layer line spacings on subsequent axial ω-oscillation photographs were equal within experimental error to those predicted by the indexing program, as well as confirming the symmetry.

Lattice parameters (reported above) were obtained by a least-squares refinement of the precise $\pm 2\theta (|2\theta| > 25°)$ measurements of 14 strong independent reflections at 27°C using graphite-monochromated Mo-K_α radiation (λ 0.70954 Å).

Collection and reduction of X-ray intensity data

Data were collected at 27°C on an automated four-circle diffractometer described previously by Rohrbaugh and Jacobson [8]. All data within a 2θ sphere of 50° (11,386 reflections) in the hkl, $hk\bar{l}$, $h\bar{k}l$, and $h\bar{k}\bar{l}$ octants were measured using an ω-stepscan technique.

As a general check on electronic and crystal stability, the intensities of five standard reflections were measured every 75 reflections. These standard reflections were not observed to vary significantly, nor the crystal to decompose throughout the entire process of data collection. The space group was uniquely determined to be $P2_1/c$ by systematic absences in the data occurring when $l = 2n + 1$ for the $h0l$ reflections and $k = 2n + 1$ for the $0k0$ reflections.

The intensity data were corrected for Lorentz and polarization effects. Since $\mu = 22.6$ cm^{-1} (transmission = 0.59 ± 0.09) no absorption correction was considered necessary. The variance in each intensity was calculated by

$$\sigma_I^2 = C_T + K_t C_B + (0.03\, C_T)^2 + (0.03\, C_B)^2,$$

where C_T and C_B represent the total and background counts, K_t is a counting time constant and the factor of 0.03 represents an estimate of non-statistical errors. The estimated deviations were calculated by the finite difference method [9]. Equivalent data were then averaged and 3658 reflections with $|F_0| > 3\sigma(F_0)$ were retained for use in subsequent structure analysis and refinement steps. During the latter stages of refinement fifteen large reflections that suffered from secondary extinction and/or counter flooding effects were removed from the data set.

Solution and refinement

Since the cell parameters and calculated density indicated the presence of eight molecules per unit cell, the structural parameters for two molecules (one asymmetric unit) had to be determined. Due to the number of atoms in the asymmetric unit the title compound appeared to be a good test case for a Patterson superposition technique we have recently devised which involves the use of two multiple vector peaks to define a structural parallelogram [10]. This new method readily revealed the positions of the four irons, the sulfurs, and one bridging carbon. The remaining atoms were found by successive structure factor [11] and electron density map calculations [12]. (The ring carbons had to be located using a sharpened electron density map.) Ring hydrogens were put in at positions 1.05 Å from the corresponding ring carbons and their isotropic temperature factors were fixed at 4.5 $Å^2$. The parameters of all 40 non-hydrogen atoms were refined via a block diagonal least-squares refinement [11], minimizing the function $\omega(|F_0| - |F_c|)^2$ where $\omega = 1/\sigma_F^2$. A final full-matrix least-squares refinement was done 20 atoms (one molecule) at a time to keep the computing requirements more manageable. This refinement converged to a conventional crystallographic residual, $R = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, of 0.070. The scattering factors used for non-hydrogen atoms were those of Hanson et al. [13], modified for the real and imaginary parts of anomalous dispersion [14]. The scattering factor used for hydrogen was that of Stewart et al. [15]. The final positional and thermal parameters are listed in Tables 1 and 2, respectively. A list of the observed and calculated structure factors may be obtained from the authors.

Description and discussion

Computer-generated perspective [16] drawings of an individual $Cp_2Fe_2(CO)_3CS$ molecule (A) and of the unit cell containing all eight molecules are provided in Fig. 1 and Fig. 2, respectively. Tables 3 and 4 list selected interatomic distances and angles, the variations between independent molecules not being statistically significant.

The compound contains a bridging thiocarbonyl group and again demonstrates the preference, as compared to CO, of the CS group for the bridging rather than terminal position. Quick [5] suggests the bridging position should be preferred since the formation of the additional (second) Fe—CS bond compensates for any loss in C—S π-bonding. The carbonyl π-bond should be stronger than the thiocarbonyl π-bond and thus the CO should have less tendency to occupy the bridging position. Distances to the bridging carbons from the irons in the title compound appear to be quite similar to its carbonyl [6] and thiocarbonyl [1] analogs. The iron to terminal carbonyl—carbon distances, 1.745 Å (ave.), are uniformly shorter than the bridging distances, 1.91 Å (ave.), (cf. Table 3). The carbon—sulfur distance of 1.60(1) Å (ave.) is significantly longer than that found for terminal C≡S groups (1.51—1.54 Å) [17].

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TABLE 1

FINAL POSITIONAL PARAMETERS [a] FOR $(C_5H_5)_2Fe_2(CO)_3CS$

Atom	Molecule A		
	x	y	z
Fe(1)	0.51391 (7) [b]	0.02768 (8)	0.31244 (8)
Fe(2)	0.37171 (7)	−0.00637 (8)	0.16466 (7)
S	0.5180 (2)	0.1630 (2)	0.1368 (2)
O(1)	0.4352 (5)	0.1927 (5)	0.3815 (5)
O(2)	0.2465 (4)	0.1545 (4)	0.1742 (4)
O(3)	0.3540 (4)	−0.0848 (4)	0.3363 (4)
C(1)	0.4659 (6)	0.1290 (6)	0.3532 (5)
C(2)	0.2958 (5)	0.0893 (6)	0.1714 (5)
C(3)	0.3919 (5)	−0.0409 (6)	0.2917 (5)
C(4)	0.4768 (5)	0.0839 (5)	0.1913 (5)
C(1R1)	0.6554 (9)	−0.0068 (14)	0.3092 (11)
C(2R1)	0.6048 (8)	−0.1002 (10)	0.3222 (10)
C(3R1)	0.5908 (7)	−0.0888 (9)	0.4030 (8)
C(4R1)	0.6265 (8)	0.0087 (10)	0.4433 (9)
C(5R1)	0.6640 (8)	0.0528 (10)	0.3800 (14)
H(1R1)	0.6547	−0.0736	0.2779
H(2R1)	0.6130	−0.0433	0.2738
H(3R1)	0.5814	−0.0280	0.4461
H(4R1)	0.6094	−0.0589	0.4744
H(5R1)	0.6974	0.1218	0.3897
C(1R2)	0.3504 (20)	−0.0349 (10)	0.0228 (8)
C(2R2)	0.2643 (11)	−0.0579 (15)	0.0450 (12)
C(3R2)	0.2927 (12)	−0.1326 (11)	0.1041 (13)
C(4R2)	0.3873 (12)	−0.1530 (9)	0.1288 (10)
C(5R2)	0.4219 (9)	−0.0957 (12)	0.0777 (9)
H(1R2)	0.3461	0.0243	−0.0284
H(2R2)	0.1891	−0.0362	0.0259
H(3R2)	0.2487	0.0243	0.1357
H(4R2)	0.4326	−0.2059	0.1832
H(5R2)	0.4955	−0.0944	0.0781

[a] The positional parameters for all atoms are represented in fractional unit cell coordinates. [b] In this and succeeding tables estimated standard deviations are given in parentheses for the least significant figures. No standard deviation is given for the unrefined hydrogens.

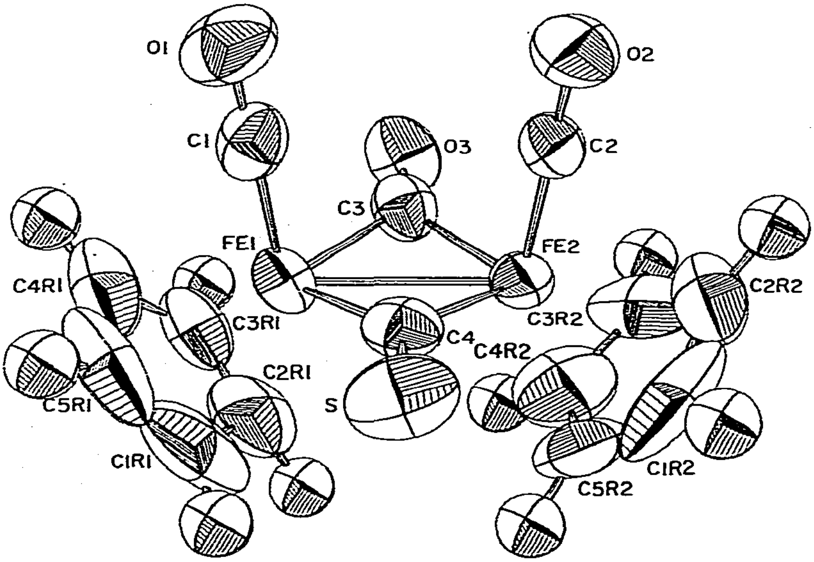

Fig. 1. View of $(C_5H_5)_2Fe_2(CO)_3CS$ molecule A.

	Molecule B		
	x	y	z
Fe(1)	0.07270 (7)	0.76860 (8)	0.25347 (7)
Fe(2)	−0.06600 (7)	0.72910 (8)	0.10433 (7)
S	−0.1335 (2)	0.8748 (2)	0.2407 (2)
O(1)	0.1229 (4)	0.9599 (4)	0.1998 (4)
O(2)	−0.0619 (5)	0.9064 (5)	0.0004 (4)
O(3)	0.1292 (4)	0.6755 (5)	0.1076 (4)
C(1)	0.1037 (5)	0.8839 (6)	0.2203 (5)
C(2)	−0.0623 (5)	0.8349 (6)	0.0412 (5)
C(3)	0.0724 (6)	0.7101 (6)	0.1384 (5)
C(4)	−0.0608 (6)	0.8077 (6)	0.2073 (5)
C(1R1)	0.0737 (10)	0.7458 (14)	0.3907 (7)
C(2R1)	0.1572 (12)	0.7882 (8)	0.3943 (7)
C(3R1)	0.2084 (7)	0.7278 (11)	0.3543 (8)
C(4R1)	0.1552 (11)	0.6454 (8)	0.3251 (7)
C(5R1)	0.0691 (10)	0.6541 (10)	0.3451 (8)
H(1R1)	0.0196	0.7751	0.4174
H(2R1)	0.1806	0.8598	0.4220
H(3R1)	0.2773	0.7431	0.3459
H(4R1)	0.1759	0.5835	0.2936
H(5R1)	0.0099	0.6028	0.3291
C(1R2)	−0.0991 (8)	0.5985 (8)	0.0223 (7)
C(2R2)	−0.0914 (8)	0.5752 (7)	0.1122 (8)
C(3R2)	−0.1623 (8)	0.6282 (8)	0.1343 (7)
C(4R2)	−0.2140 (6)	0.6880 (7)	0.0539 (10)
C(5R2)	−0.1713 (8)	0.6663 (8)	−0.0149 (7)
H(1R2)	−0.0588	0.5637	−0.0164
H(2R2)	−0.0358	0.5271	0.1604
H(3R2)	−0.1772	0.6240	0.1980
H(4R2)	−0.2750	0.7335	0.0470
H(5R2)	−0.1865	0.7159	−0.0788

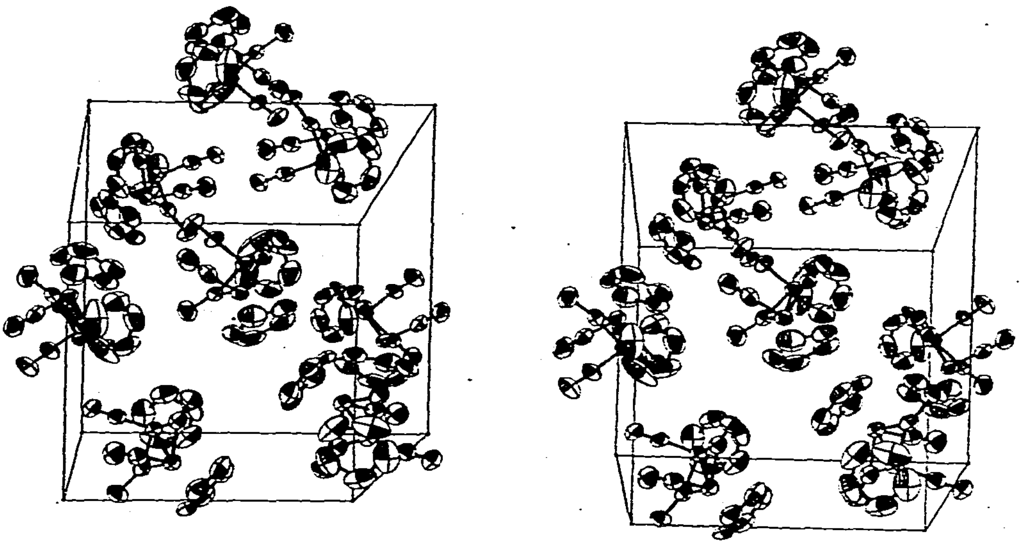

Fig. 2. Unit cell stereograph of $(C_5H_5)_2Fe_2(CO)_3CS$.

TABLE 2

FINAL THERMAL [a] PARAMETERS ($\times 10^3$) FOR $(C_5H_5)_2Fe_2(CO)_3CS$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Molecule A						
Fe(1)	4.38 (6)	5.84 (7)	5.93 (6)	−0.40 (5)	1.19 (5)	0.58 (5)
Fe(2)	4.96 (6)	5.71 (7)	5.48 (6)	0.10 (5)	1.66 (5)	−1.18 (5)
S	11.9 (2)	7.1 (2)	8.8 (2)	−0.7 (1)	6.0 (2)	1.0 (1)
O(1)	11.4 (5)	7.7 (4)	10.3 (5)	−2.4 (4)	5.2 (4)	−3.3 (4)
O(2)	8.8 (4)	8.7 (4)	7.6 (4)	3.7 (4)	2.1 (3)	0.7 (3)
O(3)	7.3 (4)	8.1 (4)	8.8 (4)	−1.6 (3)	2.7 (3)	1.8 (3)
C(1)	7.1 (5)	6.2 (5)	6.1 (5)	−2.2 (4)	2.2 (4)	0.8 (4)
C(2)	5.6 (5)	6.5 (5)	4.9 (4)	1.6 (4)	1.0 (3)	0.1 (4)
C(3)	5.8 (5)	5.5 (5)	6.5 (5)	0.1 (4)	1.3 (4)	0.3 (4)
C(4)	6.2 (5)	4.8 (4)	6.9 (5)	0.6 (4)	2.8 (4)	−0.4 (4)
C(1R1)	5.7 (7)	18.8 (17)	16.3 (13)	4.7 (9)	2.9 (8)	4.8 (12)
C(2R1)	7.4 (7)	11.5 (10)	12.4 (10)	3.8 (7)	1.7 (7)	1.5 (8)
C(3R1)	5.7 (6)	11.5 (10)	9.9 (7)	1.9 (6)	−0.2 (5)	2.2 (7)
C(4R1)	7.3 (7)	14.2 (11)	11.4 (9)	−0.2 (7)	−1.6 (6)	0.3 (8)
C(5R1)	5.2 (7)	9.4 (10)	19.8 (16)	−2.0 (6)	−0.2 (9)	2.4 (10)
C(1R2)	30 (3)	9.7 (9)	5.0 (6)	1.3 (14)	4.5 (12)	−2.3 (6)
C(2R2)	12.5 (12)	20.8 (18)	14.4 (13)	9.3 (13)	−4.4 (9)	−12.8 (12)
C(3R2)	10.6 (10)	13.9 (11)	20.0 (15)	−7.5 (9)	9.2 (11)	−12.9 (11)
C(4R2)	16.7 (13)	8.3 (8)	13.2 (11)	1.7 (8)	6.5 (10)	−2.6 (8)
C(5R2)	11.2 (10)	13.3 (12)	8.8 (8)	−2.9 (9)	6.6 (8)	−4.7 (8)
Molecule B						
Fe(1)	4.82 (6)	5.07 (6)	3.84 (5)	−0.11 (5)	1.35 (5)	0.22 (5)
Fe(2)	4.69 (6)	5.02 (7)	4.35 (6)	−0.52 (5)	1.33 (5)	0.32 (5)
S	7.4 (2)	8.0 (2)	9.5 (2)	1.6 (1)	5.0 (1)	−0.3 (1)
O(1)	7.2 (4)	5.8 (4)	8.5 (4)	−1.7 (3)	3.1 (3)	−0.4 (3)
O(2)	9.2 (5)	7.7 (4)	7.8 (4)	−0.1 (4)	1.4 (4)	3.0 (4)
O(3)	7.3 (4)	9.0 (4)	6.6 (3)	1.6 (3)	3.7 (3)	−0.4 (3)
C(1)	4.6 (4)	6.1 (5)	4.5 (4)	−0.1 (4)	1.1 (3)	−0.7 (4)
C(2)	5.4 (5)	6.8 (6)	4.3 (4)	0.0 (4)	1.1 (3)	0.4 (4)
C(3)	6.0 (5)	5.6 (5)	4.5 (4)	−0.4 (4)	1.1 (4)	1.0 (3)
C(4)	5.8 (5)	5.5 (5)	5.1 (4)	−1.0 (4)	2.3 (4)	0.5 (4)
C(1R1)	10.4 (9)	20.4 (17)	4.7 (6)	4.0 (11)	4.0 (6)	3.6 (8)
C(2R1)	15.5 (13)	10.0 (9)	3.8 (5)	0.4 (9)	−0.8 (7)	−0.3 (5)
C(3R1)	6.9 (7)	13.6 (12)	7.4 (7)	−0.8 (7)	1.0 (5)	3.9 (7)
C(4R1)	12.7 (11)	7.7 (7)	6.3 (6)	3.6 (7)	2.3 (7)	1.9 (5)
C(5R1)	11.0 (10)	11.6 (10)	5.8 (6)	−4.5 (8)	−1.4 (6)	3.7 (6)
C(1R2)	10.5 (8)	7.5 (7)	7.7 (7)	−3.6 (6)	3.1 (6)	−2.1 (6)
C(2R2)	10.3 (8)	5.8 (6)	9.2 (7)	−2.2 (6)	2.9 (6)	0.2 (5)
C(3R2)	8.9 (7)	8.2 (7)	8.6 (7)	−3.8 (6)	4.3 (6)	−0.7 (6)
C(4R2)	3.7 (5)	7.1 (7)	17.1 (11)	−1.8 (5)	1.7 (6)	−2.4 (7)
C(5R2)	8.0 (7)	9.0 (8)	7.3 (6)	−2.7 (6)	0.4 (6)	−0.1 (6)

[a] The β_{ij} are defined by: $T = \exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. For all hydrogen atoms an isotropic thermal parameter of 4.5 was assigned.

Other distances and angles in $Cp_2Fe_2(CO)_3CS$ are strikingly similar to those in its analogs except for the Fe(1)—Fe(2) distance, 2.505 Å (ave.), which is intermediate to that in *cis*-$[CpFe(CO)_2]_2$ [6], 2.531 Å, and that in *cis*-$Cp_2Fe_2(CO)_2(CS)_2$ [1], 2.482 Å. This supports any theory proposing enhancement of the bonding between the two halves of the molecule by the substitution of bridging thiocarbonyls for carbonyls.

The cyclopentadienyl rings are essentially planar, the greatest deviation from

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å)

Bonding	A	B
Fe(1)—Fe(2)	2.504 (3)	2.506 (2)
Fe(1)—C(1)	1.754 (9)	1.754 (8)
Fe(2)—C(2)	1.732 (8)	1.742 (8)
Fe(1)—C(4)	1.889 (8)	1.890 (8)
Fe(2)—C(4)	1.889 (8)	1.875 (8)
Fe(1)—C(3)	1.927 (8)	1.920 (8)
Fe(2)—C(3)	1.906 (9)	1.907 (8)
Fe(1)—cg(1) [a]	1.752	1.752
Fe(2)—cg(2)	1.749	1.750
C(1)—O(1)	1.127 (12)	1.143 (10)
C(2)—O(2)	1.150 (10)	1.155 (11)
C(3)—O(3)	1.175 (11)	1.179 (11)
C(4)—S	1.596 (9)	1.606 (9)
C(1R1)—C(2R1)	1.515 (22)	1.326 (23)
C(2R1)—C(3R1)	1.321 (21)	1.384 (21)
C(3R1)—C(4R1)	1.482 (18)	1.345 (18)
C(4R1)—C(5R1)	1.395 (25)	1.391 (22)
C(5R1)—C(1R1)	1.319 (26)	1.418 (22)
C(1R2)—C(2R2)	1.441 (35)	1.368 (17)
C(2R2)—C(3R2)	1.322 (25)	1.390 (17)
C(3R2)—C(4R2)	1.319 (23)	1.441 (16)
C(4R2)—C(5R2)	1.317 (23)	1.421 (20)
C(5R2)—C(1R2)	1.368 (23)	1.362 (15)

Non-bonding [b]	A		A
O(1A)—H(3R1A)^{II}	2.68	O(1B)—H(5R1B)^{VI}	2.66
S(A)—H(3R1A)^{III}	2.97	O(1B)—H(3R2B)^{VI}	2.68
S(A)—H(3R1B)^{III}	3.09	S(B)—H(4R1B)^{VI}	2.92
S(A)—H(4R2A)^{IV}	3.13	S(B)—H(2R2B)^{VI}	3.16
O(4A)—H(4R1A)^{II}	2.39	O(4B)—H(3R2A)^{II}	2.58
O(4A)—H(3R1B)^{I}	2.62	O(4B)—H(5R1A)^{IV}	2.60
O(2A)—H(5R2B)^{V}	2.25	O(2B)—H(2R2A)^{VII}	2.49
O(2A)—H(3R2B)^{VI}	2.51		

[a] Center of gravity of the ring. [b] Contacts are between the first atom at x, y, z and the second at the equivalent position denoted by the Roman Numerals:

I	x	y	z
II	$1 - x$	y	$1 - z$
III	$1 - x$	$0.5 + y$	$0.5 - z$
IV	$1 - x$	$-0.5 + y$	$0.5 - z$
V	$-x$	$-y$	$-z$
VI	$-x$	$0.5 + y$	$0.5 - z$
VII	$-x$	$1.5 + y$	$-z$

least-squares planarity being 0.032 Å, and assume *cis* orientation in the molecule. The C—C ring distances range from 1.319—1.515 Å, averaging 1.38 Å; the iron to ring carbon distances range from 2.06—2.14 Å, with the average distance being 2.11 Å. Such a variation is not unexpected considering the large thermal parameters and general difficulty encountered locating and refining the

TABLE 4

INTERATOMIC ANGLES (°)

	A	B
O(3)—C(3)—Fe(1)	137.8 (6)	138.4 (6)
O(3)—C(3)—Fe(2)	140.5 (6)	139.7 (6)
S—C(4)—Fe(1)	138.4 (4)	138.0 (4)
S—C(4)—Fe(2)	138.5 (4)	138.5 (4)
O(3)—C(3)—C(4)	173.8 (7)	175.4 (7)
S—C(4)—C(3)	174.2 (5)	173.1 (5)
C(3)—Fe(1)—Fe(2)	48.9 (2)	48.9 (2)
C(3)—Fe(2)—Fe(1)	49.6 (2)	49.3 (2)
C(4)—Fe(1)—Fe(2)	48.5 (2)	48.0 (2)
C)4)—Fe(2)—Fe(1)	48.5 (2)	48.5 (2)
C(3)—Fe(1)—C(4)	96.0 (3)	95.9 (3)
C(3)—Fe(2)—C(4)	96.7 (3)	96.9 (3)
Fe(1)—C(1)—O(1)	178.1 (8)	178.5 (9)
Fe(2)—C(2)—O(2)	177.9 (8)	177.9 (9)
C(1)—Fe(1)—C(4)	90.7 (4)	88.6 (3)
C(1)—Fe(1)—C(3)	89.1 (4)	91.7 (4)
C(2)—Fe(2)—C(4)	88.8 (4)	89.3 (4)
C(2)—Fe(2)—C(3)	90.1 (4)	91.7 (4)
C(1)—Fe(1)—Fe(2)	99.1 (2)	98.0 (2)
C(2)—Fe(2)—Fe(1)	98.6 (2)	98.6 (2)
Fe(1)—C(3)—Fe(2)	81.6 (4)	81.8 (4)
Fe(1)—C(4)—Fe(2)	83.0 (3)	83.5 (4)
C(1)—Fe(1)—cg(1)	125.1	124.7
C(2)—Fe(2)—cg(2)	125.5	124.9
Fe(2)—Fe(1)—cg(1)	135.7	137.2
Fe(1)—Fe(2)—cg(2)	135.9	136.5
C(3)—Fe(1)—cg(1)	121.9	121.1
C(3)—Fe(2)—cg(2)	121.6	120.6
C(4)—Fe(1)—cg(1)	124.4	125.3
C(4)—Fe(2)—cg(2)	124.4	124.7
C(1R1)—C(2R1)—C(3R1)	105.3 (12)	110.3 (12)
C(2R1)—C(3R1)—C(4R1)	110.0 (12)	107.9 (12)
C(3R1)—C(4R1)—C(5R1)	105.4 (12)	108.2 (11)
C(4R1)—C(5R1)—C(1R1)	110.5 (13)	106.9 (12)
C(5R1)—C(1R1)—C(2R1)	108.7 (15)	106.8 (14)
C(1R2)—C(2R2)—C(3R2)	104.1 (15)	108.2 (9)
C(2R2)—C(3R2)—C(4R2)	113.5 (17)	107.4 (11)
C(3R2)—C(4R2)—C(5R2)	106.4 (13)	106.0 (9)
C(4R2)—C(5R2)—C(1R2)	104.7 (15)	107.8 (10)
C(5R2)—C(1R2)—C(2R2)	110.9 (16)	110.7 (11)

ring carbons and is probably indicative of considerable freedom of motion.

The bridging groups in the molecule are bent away from the cyclopentadienyl rings via a folding along the Fe—Fe bond. The dihedral angle between the least-squares planes of Fe(1)—C(3)—O(3)—Fe(2) and Fe(1)—C(4)—S—Fe(2) is 14.45° in molecule A and 12.93° in molecule B, the difference being likely, due to packing forces. Additional dihedral and torsional angles of interest are included in Table 5.

The packing seems to be Van der Waals in nature with few short approaches between terminal oxygen or sulfurs and hydrogens (Table 2). Furthermore these short distances seem to have little bearing on the structure as evidenced by the close correspondence between the structural features of the two independent molecules in the asymmetric unit and by similarities to its analogs.

TABLE 5

SELECTED DIHEDRAL ANGLES AND LEAST SQUARES PLANES [a]

Planes defined by Fe(1), Fe(2), C(3), O(3), C(4), S
A: $(0.60210)x + (-0.77433)y + (-0.19461)z = 2.14646$
B: $(-0.33724)x + (-0.84827)y + (0.40827)z = 4.08255$

Atom	Distance from plane (Å)	
	A	B
Fe(1)	0.1846	0.1611
Fe(2)	0.1842	0.1630
C(3)	−0.0338	−0.0353
O(3)	−0.1678	−0.1488
C(4)	−0.0092	0.0121
S	−0.1579	−0.1522

Plane	Defined by
1	Fe(1), Fe(2), C(3), O(3)
2	Fe(1), Fe(2), C(4), S
3	C(1R1)—C(5R1)
4	C(1R2)—C(5R2)
5	Fe(1), Fe(2), C(3), C(4)

Plane	Plane	Dihedral Angle (°)	
		A	B
1	2	14.45	12.93
3	5	47.50	47.78
4	5	47.65	47.65

	Torsional Angles (°)	
	A	B
C(1), Fe(1), Fe(2), C(2)	2.03	0.05
O(3), C(3), Fe(1), C(1)	−80.17	84.38
O(3), C(3), Fe(2), C(2)	82.92	−83.62
S, C(4), Fe(1), C(1)	82.24	−78.30
S, C(4), Fe(2), C(2)	−81.29	78.15

[a] Planes are defined by $c_1X + c_2Y + c_3Z - d = 0$, where X, Y, and Z are Cartesian coordinates which are related to the triclinic cell coordinates (x, y, z) by the transformations:
$X = xa\sin\gamma + zc\{(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma\} = xa + zc\cos\beta$
$Y = xa\cos\gamma + yb + zc\cos\alpha = yb$
$Z = zc\{(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}/\sin\gamma\} = zc\sin\beta$

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