that such splitting can be detected under high resolution.[18]

It is of interest that, in each case, the resonance due to the cyclopentadienyl protons appears at a higher field than the signal reported for the parent $C_5H_5Fe(CO)_2(COCH_3)$. This shift may result from replacement of CO by the more basic phosphines or phosphites which would place higher electron density on the ring. Surprisingly, however, no systematic relationship appears to exist between the basicity of the phosphorus-containing ligand and the chemical shift of the cyclopentadienyl (and acetyl) protons.

The complexes prepared in this study contain four different groups bonded to iron; in this respect they resemble the cyclopentadienylcobalt[19] and -rhodium[20] carbonyl derivatives, $C_5H_5M(CO)(R_F)I$ (M = Co, Rh; $R_F = CF_3, C_2F_5, C_3F_7$), and the methoxycarbonyl compound of manganese, $C_5H_5Mn(CO)(NO)(COOCH_3)$.[21] Since the arrangement of four groups around the metal is in all probability "tetrahedral,"[22] it should be possible to effect resolution of these organometallic racemates into their respective enantiometers. This, however, has not been attempted in our study.

Acknowledgment.—Support of this research by a grant from The Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[18] High-resolution nmr spectra of the isomeric $[C_5H_5Fe\{P(CH_3)_2\}(CO)]_2$ show that the cyclopentadienyl resonances are triplets due to coupling of the cyclopentadienyl protons with the two equivalent phosphorus nuclei; see R. G. Hayter, *J. Am. Chem. Soc.*, **85**, 3120 (1963).

[19] R. B. King, P. M. Treichel, and F. G. A. Stone, *ibid.*, **83**, 3593 (1961).

[20] J. A. McCleverty and G. Wilkinson, *J. Chem. Soc.*, 4200 (1964).

[21] R. B. King, M. B. Bisnette, and A. Fronzaglia, *J. Organometal. Chem.* (Amsterdam), **4**, 256 (1965).

[22] The existence of optical isomers of $C_5H_5Rh(CO)(C_2F_5)I$ has been demonstrated by X-ray crystallography; see M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).

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Syntheses of Some Cyclopentadienyl Transition Metal Sulfides and the Crystal Structure of $(C_5H_5FeS)_4$

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From the reactions of $C_5H_5V(CO)_4$ and $[C_5H_5Fe(CO)_2]_2$ with S_8, the cyclopentadienyl metal sulfides $[(C_5H_5)_2V_2S_5]_n$ and $(C_5H_5FeS)_4$, respectively, have been isolated. $[(C_5H_5)_2V_2S_5]_n$ is also obtained from $C_5H_5V(CO)_4$ and cyclohexene sulfide, while $[C_5H_5Mo(CO)_3]_2$ and cyclohexene sulfide produce $[C_5H_5MoS_2C_6H_{11}]_n$. $(C_5H_5FeS)_4$ crystallizes in both an orthorhombic and a monoclinic phase, respectively characterized by: space group Pnam, with $a = 17.444$ A, $b = 10.488$ A, $c = 11.348$ A, $Z = 4$; and space group C2/c or Cc, with $a = 18.787$ A, $b = 7.676$ A, $c = 15.073$ A, $\beta = 108.94°$, $Z = 4$. The crystal structure of the former phase, refined to $R = 5.8\%$, shows the molecule to consist of an elongated tetrahedron of iron atoms with a sulfur atom above each face and a cyclopentadienyl ring projecting from each corner. The molecular symmetry is exactly m (C_s) or approximately $\bar{4}2m$ (D_{2d}). Two interiron bonds of lengths 2.644 and 2.618 A, four independent Fe–S bonds averaging 2.206 A, and three independent Fe–S bonds averaging 2.256 A are present. Final refinement of the cyclopentadienyl rings by the Lipscomb–King hindered-rotor approximation resulted in an R of 6.9%.

Introduction

The reactions of organic disulfides and mercaptans with metal carbonyl and cyclopentadienyl metal carbonyl compounds have been widely explored. Examples of products isolated from such reactions are $[C_5H_5Fe(SCH_3)(CO)]_2$,[2] $[C_5H_5V(SCH_3)_2]_2$,[3] $[Mn(CO)_4(SR)]_2$,[4] and $[Fe(CO)_3(SR)]_2$.[5] The reactions of elemental sulfur with such metal compounds have been less thoroughly explored; a few metal carbonyl derivatives such as $Co_3(CO)_9S$[6] and $Co_2Fe(CO)_9S$[7] have been prepared *via* reactions involving S_8. The only reported reaction of S_8 with a cyclopentadienyl metal compound is that with $(C_5H_5)_3Mn_2(NO)_3$ to give the unusual product $[C_5H_5Mn(NO)S_2]_6$.[8]

The reactions of several cyclopentadienyl metal carbonyl compounds with sulfur were thus pursued in a search for additional cyclopentadienyl metal sulfide derivatives. Cyclohexene sulfide was also investigated as a potential source of reactive sulfur.

Several of the new compounds doubtless are oligomeric and representative of a general class of polynucleates containing extensive bonding between the constituent nuclei. The crystal structure of one of these materials, $(C_5H_5FeS)_4$, was determined to examine the stereochemical principles displayed by such polynucleates.

[1] Contribution No. 1124.

[2] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).

[3] R. H. Holm, R. B. King, and F. G. A. Stone, *Inorg. Chem.*, **2**, 219 (1963).

[4] P. M. Treichel, J. H. Morris, and F. G. A. Stone, *J. Chem. Soc.*, 720 (1963).

[5] R. B. King, *J. Am. Chem. Soc.*, **84**, 2460 (1962).

[6] L. Marko, G. Bor, and E. Klumpp, *Chem. Ind.* (London), 1491 (1961).

[7] S. A. Khattab, L. Marko, G. Bor, and B. Marko, *J. Organometal. Chem.*, **1**, 373 (1964).

[8] T. S. Piper and G. W. Wilkinson, *J. Am. Chem. Soc.*, **78**, 900 (1956).

Experimental Section

Reagents.—All reactions were performed in glass apparatus in a dry, oxygen-free nitrogen atmosphere. $[C_5H_5Fe(CO)_2]_2$ and $[C_5H_5Mo(CO)_3]_2$ (Alfa Inorganics, Inc.) and $C_5H_5Mn(CO)_3$ (Ethyl Corp.) were used as obtained. $[C_5H_5Ni(CO)]_2$ and $(C_5H_5)_3Ni_3(CO)_2$ were prepared as described in the literature.[9] The literature preparation[10] of $C_5H_5V(CO)_4$ was modified in that the solution containing $(C_5H_5)_2V$ was evaporated and the dry residue carbonylated at 1000 atm and 130° for 12 hr. Yields of 35–40% were consistently obtained by this procedure.

Cyclohexene sulfide (Aldrich Chemicals) and sulfur (Mallinckdrodt, sublimed) were used without purification. All solvents were dried by standard techniques before use.

Spectra.—Infrared spectra of KBr wafers were recorded on a Perkin-Elmer Model 21 spectrophotometer from 2 to 15 μ and on a Perkin-Elmer Model 137 KBr Infrared spectrophotometer from 13 to 25 μ.

Preparation of $[C_5H_5FeS]_4$.—In a nitrogen atmosphere, a solution of $[C_5H_5Fe(CO)_2]_2$ (20.0 g, 56.5 mmoles) and S_8 (5.2 g, 20.2 mmoles) in 500 ml of toluene was refluxed for 16 hr. After cooling to room temperature, the solution was filtered in air and the black solid washed with petroleum ether and air dried. This crude product (16 g) was extracted with three 250-ml portions of hot bromobenzene, and the extracts were stored at 5° overnight to give 7.0 g (38%) of black crystalline $(C_5H_5FeS)_4$. Concentration of the filtrate gave an additional 4.5 g of less pure product for a total of 11.5 g (62%). Recrystallization from bromobenzene (7.0 g/450 ml) in a nitrogen atmosphere gave 4.3 g of mixed monoclinic and orthorhombic black crystals, dec 230–240°. *Anal.* Calcd for C_5H_5FeS: C, 39.2; H, 3.3; Fe, 36.2; S, 21.0. Found: C, 39.7; H, 3.6; Fe, 36.7; S, 20.9.

$(C_5H_5FeS)_4$ is stable to oxygen and water in the solid state but slowly decomposes in solution. The solubility in organic solvents is quite low and the tetrameric nature was discovered only as a result of the crystal structure analysis. The compound is diamagnetic with a diamagnetic susceptibility of -0.069×10^{-6} emu/g at room temperature as measured on a Gouy balance.

The infrared spectrum of a mixture of the monoclinic and orthorhombic forms (KBr pellet) showed bands at 3086 (m), 1653 (w), 1418 (s), 1351 (m), 1266 (w), 1111 (m), 1064 (m), 1013 (sh), 1016 (s), 1000 (s), 901 (w), 886 (w), 850 (m), 840 (sh), 883 (s), 822 (s), 809 (s), 796 (s), 585 (w), 442 (m), and 408 (m, br) cm^{-1}.

Attempted Isolation of an Intermediate in the Preparation of $[C_5H_5FeS]_4$.—$[C_5H_5Fe(CO)_2]_2$ (10.6 g, 30 mmoles), S_8 (2.0 g, 15 mmoles), and 400 ml of benzene were refluxed for 2.0 hr in a nitrogen atmosphere. The infrared spectrum of this solution showed a trace of a bridge carbonyl absorption at 1780 cm^{-1} and intense terminal carbonyl bands at 1990 and 2040 cm^{-1}. The mixture was cooled and filtered, and the red-brown filtrate was applied to a 2.5 × 40 cm chromatographic column made up of grade 1 neutral alumina (Woelm). Elution with benzene gave a dark red eluate which was evaporated to a dark red oil. Numerous attempts to crystallize this oil were unsuccessful. The oil showed carbonyl stretching frequencies at 2041 (s) and 1992 (s) cm^{-1} in dichloromethane solution and appeared to be stable to oxygen and water.

Preparation of $[(C_5H_5)_2V_2S_5]_n$.—In a nitrogen atmosphere, a solution of $C_5H_5V(CO)_4$ (6.4 g, 28.1 mmoles) and S_8 (1.8 g, 7.0 mmoles) in 400 ml of toluene was refluxed for 16 hr. The resulting dark brown solution was cooled and the solvent removed under vacuum to give 3.7 g of a dark brown, carbonyl-free solid. This air-stable crude product was extracted with a total of 950 ml of benzene and the filtered extract chromatographed in two portions on 2.5 × 40 cm columns of grade 2 neutral alumina (Woelm). No precautions for the exclusion of oxygen were taken during this procedure. The large volume was necessary owing to the low solubility of the product in benzene, and a black eluate was obtained even before all of the original solution had run onto the column. Upon elution with benzene, all of the black band was eluted and green and brown bands remained on the column. Further elution with dichloromethane, acetone, and ethanol failed to move these impurity bands. The combined black eluates were evaporated on a rotary evaporator and the residue (3.2 g) was crystallized from 200 ml of toluene in a nitrogen atmosphere to give 2.5 g (45%) of brown-black crystalline $[(C_5H_5)_2V_2S_5]_n$, mp 309–312° dec. *Anal.* Calcd for $C_{10}H_{10}S_5V_2$: C, 30.6; H, 2.6; V, 26.0; S, 40.8. Found: C, 31.3; H, 2.7; V, 26.6; S, 40.9. Low solubility precluded a solution molecular weight determination.

The same product is obtained if cyclohexene sulfide is used instead of S_8 in the above procedure.

$[(C_5H_5)_2V_2S_5]_n$ is an air- and water-stable solid whose solutions are slowly decomposed on standing in contact with oxygen. The compound has low solubility in organic solvents and is decomposed by dilute acid or base. The compound sublimes with some decomposition at 200° (0.1 μ) and was shown to be diamagnetic using a Faraday microbalance.

The infrared spectrum (KBr pellet) showed bands at 3096 (m), 1653 (w), 1439 (m), 1429 (m), 1361 (w), 1064 (m), 1020 (sh), 1010 (m), 920 (w, br), 836 (sh), 813 (s), 562 (m), 526 (s), 465 (w, br), and 422 (w, br) cm^{-1}.

The proton magnetic resonance spectrum was recorded on a Varian A-60 spectrometer in saturated $CDCl_3$ solution and showed a weak sharp line at τ 3.32 referred to $(CH_3)_4Si$ as an external standard.

Other Reactions with S_8.—When S_8 and $[C_5H_5Mo(CO)_3]_2$ were refluxed in benzene for 16 hr, a brown carbonyl-free solid was obtained which was insoluble in a wide range of solvents and could not be purified. Analyses of the crude product showed it to contain C, H, S, and Mo, but an empirical formula could not be reliably determined.

Refluxing a solution of $C_5H_5Mn(CO)_3$ and S_8 in benzene while irradiating with either a low-pressure mercury ultraviolet lamp or a General Electric RS 275 sunlamp produced a precipitate of amorphous sulfur. Subsequently $C_5H_5Mn(CO)_3$ was recovered unchanged.

Preparation of $[C_5H_5MoS_2C_6H_{11}]_n$.—In a nitrogen atmosphere, a solution of $[C_5H_5Mo(CO)_3]_2$ (6.0 g, 12.2 mmoles) and cyclohexene sulfide (12.0 g, 11.5 mmoles) in 250 ml of benzene was refluxed for 20 hr. On cooling the solution, the brown crystalline solid which had formed was collected by filtration in air, washed well with benzene, and dried at 75° (0.5 μ) for 16 hr. This crude product (6.0 g) was crystallized twice from toluene (6.0 g/300 ml) to give 4.0 g (47%) of $(C_5H_5MoS_2C_6H_{11})_n$, mp 250–260° dec. *Anal.* Calcd for $C_{11}H_{16}MoS_2$: C, 42.9; H, 4.9; Mo, 31.2; S, 20.8. Found: C, 43.0; H, 4.8; Mo, 31.9; S, 20.9.

The solubility of $(C_5H_5MoS_2C_6H_{11})_n$ is too low in organic solvents to determine the molecular weight by solution methods. The solid compound is oxygen- and water-stable, but solutions are very slowly decomposed upon contact with air. The compound was shown to be diamagnetic using a Faraday microbalance.

The infrared spectrum (KBr pellet) shows bands at 3096 (m), 2941 (s), 2915 (sh), 2874 (m), 1504 (w), 1460 (s), 1449 (m), 1429 (s), 1361 (w), 1333 (s), 1299 (w), 1258 (m), 1217 (s), 1195 (w), 1167 (s), 1107 (s), 1093 (sh), 1064 (m), 1026 (sh), 1002 (s), 938 (w), 904 (w), 870 (w), 836 (sh), 818 (s), 787 (s), 730 (m), 691 (w), 568 (w), 485 (s), 441 (w), and 424 (m) cm^{-1}.

Other Reactions with Cyclohexene Sulfide.—The reaction of either $[C_5H_5Ni(CO)]_2$ or $(C_5H_5)_3Ni_3(CO)_2$ with cyclohexene sulfide in refluxing benzene for 16 hr led to black insoluble solids containing C, H, Ni, and S. The carbonyl-free products were insoluble in a wide variety of solvents and could not be purified or identified.

X-Ray Data for $(C_5H_5FeS)_4$.—Block-like crystals of an orthorhombic phase of $(C_5H_5FeS)_4$ appeared during rapid cooling of a bromobenzene solution from 155° to about 100°. Slower cooling overnight to 5° produced a further crop of needles, shown to be a monoclinic phase of the same composition. Lattice parameters $a = 17.444 \pm 0.003$ A, $b = 10.488 \pm 0.002$ A, and $c =$

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[9] E. O. Fischer and C. Palm, *Chem. Ber.*, **91**, 1725 (1958).

[10] R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 100 (1963).

11.348 ± 0.002 A were determined for the orthorhombic phase at 24° in an especially accurate Straumanis-type zero-level Weissenberg camera with the use of Co Kα radiation (λ_{α_1} 1.78892 A, λ_{α_2} 1.79278 A). The monoclinic lattice parameters were similarly determined to be a = 18.787 ± 0.003 A, b = 7.676 ± 0.001 A, c = 15.073 ± 0.004 A, β = 108.94 ± 0.01°. The systematic absence of reflections $0kl$ with $(k + l)$ odd and $h0l$ with h odd suggested symmetry Pnam or Pna2$_1$ for the orthorhombic phase; the complete structure analysis shows Pnam to be correct. Similarly, systematic absences suggested C2/c or Cc as probable space groups for the monoclinic phase. Tests for a piezoelectric effect were negative for both phases. Calculated densities for the orthorhombic and monoclinic phases, assuming four molecules per cell in each case, are 1.958 and 1.977 g/cm^3, respectively. Densities measured by flotation are 1.95 and 1.98 g/cm^3.

Intensity data were measured for all 2049 independent reflections with $\sin \theta/\lambda < 0.6$ using a Picker goniometer in the moving crystal–moving counter technique.[11] Zr-filtered Mo Kα radiation was used, with a scintillation detector followed by a pulse-height analyzer set to accept about 90% of the Kα pulse distribution. A 1.67° range in 2θ was scanned in 100 sec and a 20-sec background count was made on either side of the peak. Diffractometer settings and later absorption corrections were calculated using programs written by one of the authors (C. T. P.). The crystal used for intensity collection was an elongated octahedron about 0.14 mm in average diameter. Transmission factors, evaluated by numerical integration, varied from 0.65 to 0.72. The usual Lorentz-polarization factors were applied and data brought to a common scale through use of a standard reflection monitored about every 4 hr. A standard deviation was assigned to each reflection by considering counting statistics and a 2% uncertainty in relative scale. Intensities measured as less than 2σ were considered absent and assigned threshold values of 2σ. There were 453 such "unobserved" reflections.

Structure Analysis

Solution and Ellipsoidal Thermal Refinement.—The three-dimensional Patterson function was used to obtain a trial structure. An early false start which satisfactorily explained all Fe–Fe and Fe–S vectors but which was chemically somewhat unreasonable could not be refined below R = 35% ($R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$). A second set of iron and sulfur positions was then found which gave an R factor of 25% after four least-squares cycles. Several F_o and ΔF syntheses calculated at various further stages of refinement led to location of the remaining atoms. Although this "heavy-atom" procedure is fairly straightforward, disorder in the position of one cyclopentadienyl ring seems to warrant a brief account of the evidence for disorder and steps taken to avoid bias in the Fourier syntheses. The first Fourier map, phased with the aid of Fe and S parameters, revealed the positions of all cyclopentadienyl rings, but seemed to show disorder of the cyclopentadienyl ring attached to Fe(2) (denoted Cp(2)). Cp(3), in general position, was added to the Fe and S atoms of the model; this action lowered R to 22% after three least-squares cycles. Addition of the two atoms of Cp(1) and of Cp(2) which are in general positions allowed reduction of R to 15.2%. An F_o map based on phases of all atoms included at this stage confirmed the ordered nature of Cp(1) and strengthened the evidence for an approximate $^2/_3$–$^1/_3$ disorder of Cp(2) between the two positions allowed by the mirror at $z = ^1/_4$. The preferred position was such as to aid in destruction of a pseudo-mirror at y = 0. To consider the possibility that the apparent disorder was caused by a "ghost" reflection of Cp(1) in the pseudo-mirror, an ordered model was used which allowed reduction of R to 13.2% in four least-squares cycles. A ΔF map computed at this stage using only the Fe and S atoms confirmed the reality of the disorder, as did the bond length pattern in the ordered Cp(2)—a distance of about 1.6 A across the mirror and 1.2 A between the special position atom and its neighbors. The ordered model was, however, refined through five anisotropic least-squares cycles to R = 7.3%, where it was near convergence. A $^1/_2$–$^1/_2$ disorder of Cp(2) was introduced by using four atomic sites (see Figure 1) in the ring. This model refined to R = 5.8%, where it converged. A final difference map in the ring plane indicated that the disorder is closer to 60–40%.

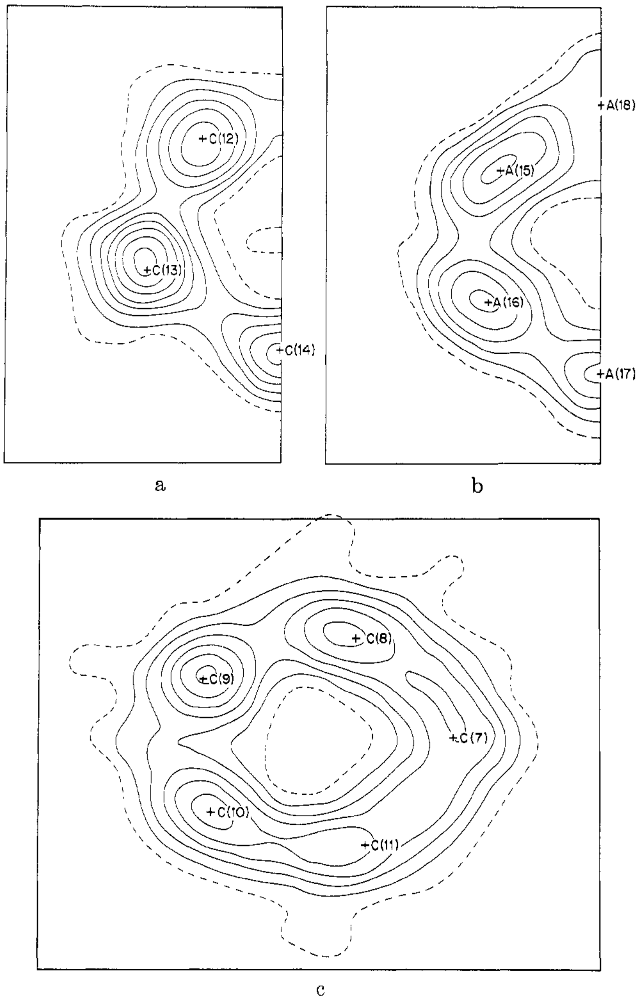

Figure 1.—Electron density in the planes of (a) Cp(1), (b) Cp(2), and (c) Cp(3). Atomic sites shown are from the least-squares refinement. A(15)–A(18) are sites of pseudo-atoms used to describe the disorder in Cp(2). A(17) was given a fractional occupancy of 0.5 to 0.67 and A(18) 0.5 to 0.33. The contours are at intervals of 1 e/A^3, with the one-electron contour dashed.

A modification of the Gantzel–Sparks–Trueblood block-diagonal least-squares program[12] was used for all

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(11) T. Furnas, "Single Crystal Orienter Instruction Manual," General Electric Co., Milwaukee, Wis., 1956.

TABLE I

FINAL STRUCTURAL PARAMETERS (FROM HINDERED ROTOR REFINEMENT)[a]

(i) Iron and Sulfur Parameters[b]

Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Fe(1)	892 (1)	1403 (1)	$^1/_4$	167 (5)	70 (1)	36 (1)	14 (2)	0	0
Fe(2)	815 (1)	−1090 (1)	$^1/_4$	177 (5)	72 (1)	37 (1)	−23 (2)	0	0
Fe(3)	2460 (1)	16 (1)	1335 (1)	167 (3)	52 (1)	50 (1)	2 (1)	−15 (1)	4 (2)
S(4)	2178 (2)	1637 (2)	$^1/_4$	194 (8)	47 (2)	55 (2)	6 (3)	0	0
S(5)	2082 (2)	−1545 (2)	$^1/_4$	223 (9)	52 (2)	56 (2)	1 (3)	0	0
S(6)	1187 (1)	127 (2)	1022 (1)	191 (5)	80 (2)	36 (1)	3 (2)	3 (1)	1 (3)

(ii) Cyclopentadienyl Parameters[c]

Ring	x	y	z	B	$\mathbf{N}\cdot\hat{\mathbf{a}}$	$\mathbf{N}\cdot\hat{\mathbf{b}}$	$\mathbf{N}\cdot\hat{\mathbf{c}}$	$\mathbf{M}\cdot\hat{\mathbf{a}}$	$\mathbf{M}\cdot\hat{\mathbf{b}}$	$\mathbf{M}\cdot\hat{\mathbf{c}}$	r	b
Cp(1)	197 (3)	2614 (5)	$^1/_4$	3.2 (1)	−0.7023	0.7119	0	0.7119	0.7023	0	1.232 (5)	2.1 (2)
Cp(2a)	4 (5)	−2080 (7)	$^1/_4$	3.1 (2)	0.7478	0.6639	0	−0.6639	0.7478	0	1.212 (8)	1.9 (2)
Cp(2b)	143 (8)	−2343 (14)	$^1/_4$	2.3 (3)	0.7478	0.6639	0	0.6639	−0.7478	0	1.232 (12)	2.3 (3)
Cp(3)	3183 (2)	−54 (5)	259 (4)	3.7 (1)	0.7094	0.0353	−0.7039	0.7044	0.0002	0.7098	1.200 (4)	0.59 (4)

[a] Standard deviations are given in parentheses and apply to the least significant digit in each case. The temperature factor is of the form $\exp -[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]$. [b] Atomic x, y, and z parameters are multiplied by 10^4. B_{11} values are multiplied by 10^5, the remainder by 10^4. [c] The ring x, y, z parameters are multiplied by 10^4. Cp(2a) and Cp(2b) are alternate positions of ring 2 and were given occupancy factors of $^2/_3$ and $^1/_3$, respectively. **N** is a unit vector normal to the plane; **M** is a unit vector running from the ring center toward one atomic site.

refinement, minimizing $\Sigma w||F_o| - |F_c||^2$. The squared reciprocal of each reflection's standard deviation was used as its weight. The Fourier summation programs were those of one of the authors (C. J. F.).

It should be noted that the choice of space group is not as unambiguous as it often is. Because the final fit of the structural model seemed satisfactory, no attempt was made to improve it by lowering the symmetry. Such a need would probably manifest itself either as unexplained peaks in the final difference maps or as excessive apparent thermal motion in one or more atoms. The former effect is absent; the latter, corresponding to very slight deviation from mirror symmetry, is present essentially only in Cp(3) and is explicable on packing grounds. It is thus very probable that Pnam is the correct space group and it is certain that deviations from this symmetry are at most small.

The Cyclopentadienyl Groups as Hindered Rotors.—The rather broad range of C–C bond lengths in the cyclopentadienyl groups (1.34–1.46 A) and the large degree of vibrational motion present in these rings suggested that they should be treated as hindered rotors. The X-ray scattering by such groups has been given by King and Lipscomb.[13] It was felt that the Lipscomb–King hindered-rotor scattering expression would, in addition to describing the thermal motion more accurately than the ellipsoidal model, provide reliable measures of the cyclopentadienyl bond length without recourse to the artificial "riding" corrections often used. The hindered-rotor model requires (in the present case) assumption of a regular pentagonal ring of carbon atoms and definition of a normal vector for the ring, a vector from the ring center to one "potential minimum" or mean atomic site, a constant describing the barrier to rotation, and a value of the ring "radius" or distance from the center to an atom. The model does not allow thermal motion of the ring center of gravity or permit any out-of-place tipping of the ring. A proper description of such motion would be extremely difficult. Recourse was therefore made to a compromise in which a single isotropic B value was assigned to the ring as a whole, together with the Lipscomb–King parameters. The scattering by a cyclopentadienyl group (j) is then given by $F_{\mathrm{h_j}} = f_{\mathrm{C}}e^{-B\sin^2\theta/\lambda^2}\cdot e^{2\pi i\mathbf{h}\cdot\mathbf{k}_j}M_5(\gamma, a_j, b_j)$, where $\mathbf{h}$ is the reciprocal lattice vector $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$, $\mathbf{k}_j$ is a vector from the origin of the cell to the center of ring j, and $M_n(\gamma, a, b)$ is the Lipscomb–King M function, slightly changed in notation to make more explicit the γ functional dependence. Reference should be made to King and Lipscomb[13] for a complete definition of γ and a and of the assumptions involved; it suffices to say here that $b = V_0/2kT$, where V_0 is the height of the barrier between two minima of a rotational potential $V = 1/2V_0 \cos\phi$, and that a is a variable containing r, the "radius" of the ring, as a multiplicative constant. Together, a and γ specify the size and orientation of the ring.

It was decided in the present case to use as ring-normal and potential-minimum vectors averages determined from the final ellipsoidal refinement. The modified Gantzel–Sparks–Trueblood least-squares program[12] was further altered to permit refinement of the ring radii and potential constants.

The x, y, z, and B parameters for each ring were used to define a 4×4 matrix; r and b defined a separate 2×2 matrix. At the end of each cycle, parameters were moved by a fraction of the calculated shift, the fraction ranging from 0.3 in early cycles to 0.7 in the last. Values of the M function and its derivative were obtained by interpolation from tables calculated at the beginning of each cycle, the tabular interval being chosen to give three-figure accuracy. When the modified least-squares program had been tested, all four independent rings (including Cp(2) with disorder frequencies of $^2/_3$ and $^1/_3$) were introduced as hindered rotors, using $B = 3.0$ A^2, $b = 2.0$, and $r = 1.23$ A for each. R for this calculation was 16.5%. Six cycles of least squares reduced R to 6.9%. During this refine-

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(12) International Union of Crystallography, World List of Crystallographic Computer Programs, 1st ed, Sept 1962, program 384.

(13) M. V. King and W. N. Lipscomb, *Acta Cryst.*, **3**, 155 (1950).

TABLE II

FINAL PARAMETERS FROM ELLIPSOIDAL REFINEMENT[a]

	Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
	Fe(1)	0.08908 (7)	0.1402 (1)	$^1/_4$	0.00170 (4)	0.0070 (1)	0.00371 (8)	0.0015 (1)	0	0
	Fe(2)	0.08152 (7)	−0.1090 (1)	$^1/_4$	0.00181 (4)	0.0074 (1)	0.00375 (8)	−0.0024 (1)	0	0
	Fe(3)	0.24600 (4)	0.0016 (1)	0.1335 (1)	0.00170 (2)	0.0052 (1)	0.00508 (5)	0.0001 (1)	0.0014 (1)	0.0005 (1)
	S(4)	0.2178 (1)	0.1637 (2)	$^1/_4$	0.00200 (6)	0.0049 (2)	0.0056 (2)	0.0007 (2)	0	0
	S(5)	0.2081 (1)	−0.1546 (2)	$^1/_4$	0.00219 (7)	0.0053 (2)	0.0057 (2)	−0.0004 (2)	0	0
	S(6)	0.1188 (1)	0.0127 (1)	0.1022 (1)	0.00195 (4)	0.0079 (1)	0.00361 (8)	−0.0002 (2)	0.0003 (1)	−0.0001 (2)
	C(7)	0.3661 (4)	−0.0022 (11)	0.4017 (8)	0.0021 (2)	0.035 (2)	0.0123 (8)	0.0015 (13)	−0.0052 (7)	−0.001 (3)
	C(8)	0.3340 (4)	0.0993 (7)	0.4554 (8)	0.0047 (2)	0.0134 (8)	0.0201 (9)	−0.0086 (8)	−0.0145 (8)	0.013 (2)
Cp(3)	C(9)	0.2802 (4)	0.0584 (9)	0.5361 (6)	0.0038 (3)	0.0194 (10)	0.0080 (6)	0.0034 (9)	−0.0064 (7)	−0.008 (1)
	C(10)	0.2800 (5)	−0.0762 (8)	0.5266 (7)	0.0054 (3)	0.0189 (9)	0.0145 (7)	−0.0070 (9)	−0.0124 (8)	0.023 (1)
	C(11)	0.3323 (5)	−0.1078 (8)	0.4439 (9)	0.0057 (3)	0.0146 (8)	0.0244 (11)	0.0113 (8)	−0.0177 (9)	−0.014 (2)
	C(12)	−0.0206 (3)	0.1939 (6)	0.3126 (6)	0.0024 (2)	0.0113 (7)	0.0099 (7)	0.0053 (6)	0.0010 (6)	0.001 (1)
Cp(1)	C(13)	0.0354 (4)	0.2873 (6)	0.3528 (6)	0.0031 (2)	0.0098 (6)	0.0098 (7)	0.0056 (6)	0.0021 (7)	0.003 (1)
	C(14)	0.0692 (5)	0.3411 (8)	$^1/_4$	0.0030 (4)	0.0076 (8)	0.0132 (12)	0.0046 (9)	0	0
	A(15)	0.0347 (4)	−0.2711 (6)	0.3274 (7)	0.0036 (2)	0.0111 (7)	0.0155 (8)	−0.0075 (7)	−0.0044 (8)	0.012 (1)
Cp(2)	A(16)	−0.0174 (4)	−0.1742 (7)	0.3363 (8)	0.0035 (2)	0.0144 (8)	0.0144 (8)	−0.0088 (7)	0.0076 (7)	−0.007 (1)
	A(17)	−0.0462 (9)	−0.122 (1)	$^1/_4$	0.0020 (5)	0.006 (1)	0.008 (2)	−0.006 (1)	0	0
	A(18)	−0.061 (1)	−0.323 (2)	$^1/_4$	0.004 (1)	0.015 (3)	0.030 (5)	−0.008 (3)	0	0

[a] Figures in parentheses are standard deviations applicable to the final digit tabulated in each case. "Atoms" 17 and 18 are alternate sites for the special-position atom of Cp(2) and were given occupancies of $^1/_2$ each in the last refinement cycle. A(15) and A(16) are average sites of the disordered general-position atoms of Cp(2). The temperature factor is of the form $\exp -[B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl]$.

ment, the Fe and S parameters changed by negligible amounts; the ring parameters changed to those in Table I.

Atomic parameters at the conclusion of refinement, with their standard deviations calculated by inversion of the least-squares matrices, are given in Table I. Parameters from the conclusion of the normal refinement are given in Table II for comparison. Figure 2 gives interatomic distances obtained from the hindered-rotor treatment. Angles are given in Table III. The observed structure factors and those calculated with the aid of the hindered-rotor model are presented in Table IV.

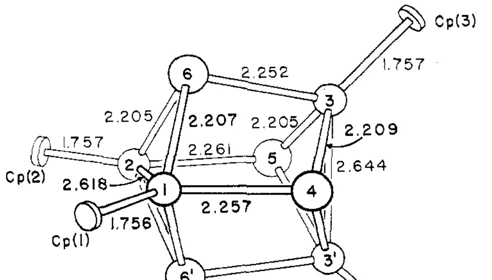

Figure 2.—Molecular structure and bond lengths in $(C_5H_5FeS)_4$. Smaller circles represent iron, larger ones sulfur, and disks the centers of cyclopentadienyl rings. The Fe(2)–Cp(2) distance is the weighted average of those for Fe(2)–Cp(2a) and Fe(2)–Cp(2b).

Discussion

Synthetic Aspects.—The new compounds $(C_5H_5FeS)_4$, $[(C_5H_5)_2V_2S_5]_n$, and $[C_5H_5MoS_2C_6H_{11}]_n$ appear to have little in common except that the iron and vanadium compounds are definitely polynuclear and the molybdenum compound is most likely polynuclear also. The infrared spectra of these compounds provide very little useful structural information other than establishing the presence of the cyclopentadienyl group. The presence of a strong absorption at 491 cm^{-1} in the spectrum of $[C_5H_5Mn(NO)S_2]_6$ has been used[8] to infer the presence of a S–S bond. Although the vanadium and molybdenum compounds show strong absorptions at 526 and 485 cm^{-1}, respectively, even tentative assignments of these bands to a S–S stretching frequency cannot be made in the absence of supporting structural data.[14–16] It is of interest to note the absence of a band in this region in the spectrum of $(C_5H_5FeS)_4$, which definitely has no S–S bonds.[17]

TABLE III

BOND ANGLES IN $(C_5H_5FeS)_4$,[a] DEG

Fe(1)–S(6)–Fe(3)	98.1	S(6)–Fe(1)–Fe(2)	53.6
Fe(2)–S(6)–Fe(3)	98.1	S(6)–Fe(2)–Fe(1)	53.6
Fe(1)–S(4)–Fe(3)	97.9	S(4)–Fe(3)–Fe(3′)	53.2
Fe(2)–S(5)–Fe(3)	97.8	S(5)–Fe(3)–Fe(3′)	53.2
Fe(1)–S(6)–Fe(2)	72.8	Fe(2)–Fe(1)–Cp(1)	133.4
Fe(3)–S(4)–Fe(3′)	73.5	Fe(1)–Fe(2)–Cp(2)	135.2
Fe(3)–S(5)–Fe(3′)	73.7	Fe(3′)–Fe(3)–Cp(3)	131.8
S(6)–Fe(1)–S(6′)	98.9	S(4)–Fe(1)–Cp(1)	127.4
S(6)–Fe(2)–S(6′)	99.0	S(5)–Fe(2)–Cp(2)	125.5
S(4)–Fe(3)–S(5)	98.4	S(6)–Fe(3)–Cp(3)	127.2
S(4)–Fe(1)–S(6)	80.4	S(6)–Fe(1)–Cp(1)	126.9
S(5)–Fe(2)–S(6)	80.5	S(6)–Fe(2)–Cp(2)	127.4
S(4)–Fe(3)–S(6)	80.5	S(4)–Fe(3)–Cp(3)	127.4
S(5)–Fe(3)–S(6)	80.7	S(5)–Fe(3)–Cp(3)	126.9
S(4)–Fe(1)–Fe(2)	99.2		
S(5)–Fe(2)–Fe(1)	99.2		
S(6)–Fe(3)–Fe(3′)	99.1		

[a] The position used for Cp(2) is the average of the two positions given in Table I.

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(14) Comparison of the infrared spectra of $(CH_3S)_2Fe_2(CO)_6$ and $S_2Fe_2(CO)_6$ in the 450–550 cm^{-1} region[15] shows the latter to have an additional band of medium intensity at 472 cm^{-1}. The presence of a S–S bond in the latter compound has been established by X-ray analysis.[16] Unfortunately, the presence of numerous Fe–C stretching vibrations in the same region renders a conclusive assignment of the 472 cm^{-1} band as a S–S stretching frequency impossible.

(15) R. A. Schunn, unpublished results.

(16) C. H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965).

(17) Similarly, the compounds $[C_5H_5V(SCH_3)_2]_2$ and $[C_5H_5Mo(SCH_3)_2]_2$ show no infrared absorptions in the 450–550 cm^{-1} region.[15]

TABLE IV

FINAL OBSERVED AND CALCULATED STRUCTURE FACTORS[a]

		0	
0	2	2717	-2603
0	4	225	294
0	6	1781	-1780
0	8	2291	2342
0	10	1092	-1127
0	12	465	477
0	14	575	-600
0	16	368	-600
1	1	165*	-253
1	3	114	39
1	5	97	-103
1	7	146	143
1	9	80	-61
1	11	-88	26
1	13	-170	-49
1	15	122	36
2	0	2199	2200
2	2	1747	1793
2	4	2113	-2118
2	6	299	-332
2	8	840	784
2	10	308	311
2	12	424	-430
2	14	-91	-20
3	1	336	322
3	3	530	-609
3	5	327	287
3	7	133	-123
3	9	190	231
3	11	211	-203
3	13	97	57
3	15	-155	-47
4	0	160	257
4	2	1559	1590
4	4	3490	-3807
4	6	1290	1287
4	8	219	-156
4	10	815	835
4	12	796	-801
4	14	377	395
5	1	194	205
5	3	693	-714
5	5	381	407
5	7	76	-84
5	9	218	217
5	11	241	-222
5	13	100	66
6	0	2052	2112
6	2	895	-932
6	4	902	-884
6	6	520	-503
6	8	996	1023
6	10	167	-174
6	12	-101	-17
6	14	-120	-132
7	1	752	-756
7	3	75*	281
7	5	331	-341
7	7	534	516
7	9	183	-167
7	11	122	94
7	13	197	-210
8	0	1439	1494
8	2	371	-347
8	4	518	-495
8	6	380	-407
8	8	824	834
8	10	181	-228
8	12	106	-16
9	1	310	-314
9	3	-81	22
9	5	172	-172
9	7	465	436
9	11	94	27
10	0	564	609
10	2	310	311
10	4	883	-881
10	6	278	292
10	8	204	152
11	1	-85	68
11	3	445	-424
11	5	348	337
11	7	96	-88
11	9	171	177
12	0	572	555
12	2	-91	-98
12	4	294	-313
12	6	-93	-56
12	8	340	305
13	1	-94	16
13	3	215	-192
13	5	-183	51
13	7	126	36
14	0	335	299
14	2	-96	-57
14	4	239	-252
16	0	158	299
		1	
1	0	1657	1663
1	1	3101	-3288
1	2	1612	-1541
1	3	802	-789
1	4	499	462
1	5	477	400
1	6	1067	-1022
1	7	1641	1646
1	8	801	797
1	9	897	-899
1	10	183	-166
1	11	-103	119
1	12	372	360
1	13	-100	-90
1	14	386	-392
1	15	168	198
2	0	-80	-84
2	1	245	283
2	2	87	13
2	3	175	-179
2	4	69	102
2	5	-61	-1
2	6	-72	65
2	7	-90	-32
2	8	-97	-50
2	9	172	168
2	10	-154	-42
2	11	132	-112
2	12	101	-10
2	13	164*	-27
3	0	655	-670
3	1	371	-341
3	2	1393	1356
3	3	2479	-2496
3	4	1220	-1220
3	5	3008*	2323
3	6	320	380
3	7	74	92
3	8	329	-337
3	9	191	183
3	10	642	618
3	11	682	-695
3	12	276	-307
3	13	461	455
4	1	331	314
4	2	402	-387
4	3	720	-723
4	4	401	424
4	5	463	513
4	6	146	-171
4	7	120	-112
4	8	118	98
4	9	147	126
4	10	123	-205
4	11	-101	-152
4	12	138	105
5	0	163	-75
5	1	902	-893
5	2	907	915
5	3	1167	-1132
5	4	817	-819
5	5	1086	1130
5	6	305	296
5	7	525	550
5	8	303	-350
5	9	360	-342
5	10	520	502
5	11	324	-339
5	12	182	-204
6	0	356	-350
6	8	132	-129
6	9	-92	143
6	10	-117	-59
6	11	-93	-91
7	0	998	935
7	1	1506	-1545
7	2	391	-414
7	3	208	-228
7	4	166	139
7	5	93	150
7	7	754	773
7	8	382	371
7	9	737	-790
7	10	-203	-108
7	11	-92	49
8	0	486	-460
8	1	422	-415
8	2	129	191
8	3	137	146
8	4	114*	-26
8	5	300	-332
8	6	278	261
8	7	444	466
8	8	264	-238
8	9	232	-247
8	10	-93	49
9	0	204	185
9	1	396	-417
9	2	78	-124
9	3	797	-792
9	4	-86	83
9	5	548	557
9	6	334	-344
9	7	-87	91
9	8	218	207
9	9	215	-203
10	0	-89	-84
10	1	124	-101
10	2	86	-80
10	3	134	-146
10	4	261	218
10	5	-90	43
10	6	-90	22
10	7	-90	48
10	8	-150	-12
11	0	-92	82
11	1	343	-349
11	2	-89	72
11	3	433	-425
11	4	204	-235
11	5	367	380
11	6	-95	98
12	0	-218	-63
12	1	140	134
12	2	-94	-93
12	3	264	-261
13	0	-101	-7
14	0	-186	-123
		2	
0	0	1422	-1358
0	1	2811	-2868
0	2	1935	-1641
0	3	1735	1566
0	4	730	754
0	5	1284	-1219
0	6	110	-156
0	7	1732	1751
0	8	785	-715
0	9	802	-849
0	10	258	275
0	11	397	396
0	12	488	468
0	13	684	-685
0	14	175	-182
0	15	365	375
1	0	330*	-369
1	1	-79	62
1	2	65	82
1	3	-126	-14
1	4	-82	-36
1	5	-124	31
1	6	171	142
1	7	-90	-11
1	8	134	-150
1	9	-101	26
1	10	86	70
1	11	81	-15
1	12	-94	-47
1	13	-114	-1
1	14	-101	34
1	15	-103	-2
2	0	3060	-3077
2	1	-79	-45
2	2	130	-78
2	3	839	-799
2	4	1824	1772
2	5	162	187
2	6	962	-947
2	7	349	332
2	8	444	-479
2	9	233	215
2	10	282	319
2	11	329	-343
2	12	442	439
2	13	155	-159
3	0	-67	-66
3	1	211	258
3	2	182	-236
3	3	127	-78
3	4	351	310
3	5	71	91
3	6	69	-60
3	7	65	-83
3	8	126	128
3	9	104	104
3	10	218	-222
3	11	104	-55
3	12	129	72
3	13	120	16
4	0	1188	-1186
4	1	791	797
4	2	545	514
4	3	2044	-2013
4	4	944	885
4	5	1085	1052
4	6	105	32
4	7	519	-562
4	8	754	-759
4	9	767	754
4	10	381	355
4	11	678	-672
4	12	239	232
5	0	214	259
5	1	217	206
5	2	435	-454
5	3	184	-175
5	4	516	545
5	5	125	164
5	6	139	-98
5	7	128	-125
5	8	89	127
5	9	-103	87
5	10	285	-284
5	11	-103	-53
5	12	87	108
6	0	1273	-1300
6	1	595	-593
6	2	183*	718
6	3	212	-196
6	4	576	592
6	5	278	-305
6	6	162	168
6	7	580	548
6	7	563	548
6	8	852	-869
6	9	-92	-28
6	10	468	485
6	11	-84	-20
7	0	585	-602
7	1	133	-162
7	2	283	286
7	3	113	180
7	4	94	-76
7	5	140	-175
7	6	379	383
7	7	-83	26
7	8	272	-273
7	9	109	-12
7	10	-93	39
7	11	-93	40
8	0	562	-588
8	1	595	-603
8	2	83	-133
8	3	118	139
8	4	938	962
8	5	217	-218
8	6	479	-494
8	7	565	549
8	8	190	-187
8	9	200	-109
8	10	96	28
9	0	480	-503
9	1	163	-128
9	2	161	194
9	3	222	204
9	4	-147	-111
9	5	312	-294
9	6	350	340
9	7	135	186
9	8	200	-212
9	9	176	-135
10	0	257	-256
10	1	-100	55
10	2	237	-261
10	3	288	-278
10	4	666	661
10	5	221	213
10	6	344	-316
10	7	149*	62
11	0	-92	28
11	1	-90	70
11	2	270	-259
11	3	108	-92
11	4	297	309
11	5	-87	117
11	6	-159	-57
12	0	657	-627
12	1	-96	-62
12	2	258	277
12	3	115	-86
13	0	-103	12
14	0	255	-258
		3	
1	0	358*	250
1	1	103	116
1	2	945	900
1	3	334	403
1	4	356	349
1	5	1974	-1964
1	6	503	463
1	7	464	469
1	8	428	-461
1	9	402	435
1	10	105	-118
1	11	147	132
1	12	94	-90
1	13	727	-751
1	14	194	162
1	15	117	199
2	0	68	14
2	1	276	254
2	2	143	-88
2	3	162	75
2	4	-66	70
2	5	-82	-52
2	6	-62	41
2	7	132	-129
2	8	-175	24
2	9	87	99
2	10	135	-66
2	11	-88	-38
2	12	-95	-3
2	13	106	31
3	0	247	-206
3	1	395	449
3	2	713	-666
3	3	113	-86
3	4	883	822
3	5	722	-745
3	6	312	-329
3	7	268	-284
3	8	172	213
3	9	918	941
3	10	453	-433
3	11	233	-227
3	12	159	185
4	0	215	230
4	1	-79	58
4	2	413	-403
4	3	61	-38
4	4	453	479
4	5	82	72
4	6	220	-211
4	7	-97	-58
4	8	198	222
4	9	163	-162
4	10	242	-240
4	11	167	107
4	12	119	113
5	0	934	-893
5	1	1761	1781
5	2	265	-294
5	3	559	-601
5	4	-97	26
5	5	144	-181
5	6	283	302
5	7	448	-460
5	8	259	-232
5	9	1118	1133
5	10	-95	-35
5	11	388	-413
6	0	-80	28
6	1	93	9
6	2	89	-122
6	3	214	242
6	4	135	119
6	5	85	-74
6	6	101	104
6	7	147	-180
6	8	106	49
6	9	92	64
6	10	149	-153
6	11	-85	18
7	0	625	-588
7	1	303	304
7	2	149	154
7	3	418	380
7	4	153	-110
7	5	592	-592
7	6	411	415
7	7	-89	88
7	8	305	-266
7	9	481	463
7	10	-93	9
8	0	567	-569
8	1	118	149
8	2	366	379
8	3	136	110
8	4	258	-270
8	5	-100	-7
8	6	141*	423
8	7	-91	-14
8	8	271	-306
8	9	-173	-95
8	10	174	139
9	0	-94	37
9	1	113	-128
9	2	188	-153
9	3	734	743
9	4	473	480
9	5	861	-912
9	6	125	-171
9	7	379	386
9	8	-93	89
9	9	155	105
10	0	208	-198
10	1	-85	15
10	2	-104	78
10	3	146	153
10	4	-90	-56
10	5	107	11
10	6	121	163
10	7	119	-80
11	0	-93	57
11	1	379	391
11	2	-197	-69
11	3	94	29
11	4	95	94
11	5	199	-197
12	0	226	257
12	1	-155	79
12	2	332	-329
12	3	-90	51
13	0	247	-266
14	0	-104	-10
		4	
0	0	1494	1369
0	1	1163	-1044
0	2	456	-541
0	3	332	411
0	4	1002	-972
0	5	716	-642
0	6	1665	1695
0	7	520	542
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5	9	136	125
5	10	-100	-47
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6	2	246	-272
6	3	-84	-17
6	3	-104	-17
6	4	803	790
6	5	148	-174
6	6	597	-561
6	7	672	668
6	8	161	-180
6	9	90	-145
7	0	-95	-29
7	1	-138	-44
7	2	165	-188
7	3	-82	65
7	4	319	318
7	5	180	-114
7	6	-90	-46
7	7	-182	118
7	8	-90	23
7	9	-94	20
8	0	240	-290
8	2	155	-119
8	3	587	-590
8	4	614	621
8	6	387	-378
8	7	-138	-58
8	8	145*	-121
8	8	464*	-121
9	0	113	82
9	1	87	-102
9	2	179	-204
9	3	-94	23
9	4	306	286
9	5	-203	-62
9	6	-93	-75
10	0	639	-595
10	1	-95	49
10	2	266	290
10	3	352	-374
10	4	139	124
11	0	156	-185
12	0	203	-217
13	0	235	-258
		11	
1	0	248	289
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1	2	381	-401
1	3	139	164
1	4	720	724
1	5	530	-572
1	6	298	-296
1	7	202	222
1	8	-86	30
1	9	663	647
1	10	353	-323
1	11	136	-148
2	0	141	-248
2	1	-120	30
2	2	134	144
2	7	-84	-28
2	8	119	-118
2	9	-92	-10
2	10	88	45
2	11	-98	14
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3	2	500	462
3	3	203	-212
3	4	150	149
3	5	289	-285
3	6	217	224
3	7	140	-190
3	8	423	-423
3	9	724	726
3	10	-285	113
4	0	224	-257
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4	2	107	128
4	3	-81	-51
4	4	-107	-70
4	5	139	105
4	6	157	173
4	7	142	-128
4	8	-93	-103
4	9	-94	84
4	10	-139	-27
5	0	498	-556
5	1	84	114
5	2	368	388
5	4	174	-179
5	5	1001	-1028
5	6	508	490
5	7	389	351
5	8	463	-470
5	9	241	261
5	10	117	125
6	0	-120	20
6	1	90	125
6	2	123	-124
6	3	-88	-44
6	4	-89	110
6	5	93	78
6	6	117	87
6	7	-130	-88
6	8	-91	-14
6	9	84	10
7	0	289	-243
7	1	92	-39
7	2	233	-216
7	3	246	279
7	4	399	403
7	5	599	-592
7	6	185	-178
7	7	-92	157
7	8	-302	5
8	0	-98	-19
8	1	179	-174
8	2	218	-175
8	3	267	253
8	4	215	251
8	5	212	-198
8	6	112	-62
8	7	127	91
9	0	-99	76
9	1	588	616
9	2	356	-370
9	3	212	-208
9	4	335	351
9	5	-152	-10
10	0	-311	-47
10	1	-93	-59
11	0	291	-281
12	0	167	-144
13	0	-110	-143
		12	
0	0	716	720
0	1	242	231
0	2	606	-630
0	3	182	-162
0	4	-86	18
0	5	-101	-19
0	6	-93	60
0	7	219	203
0	8	537	564
0	9	273	262
0	10	785	-754
0	11	-92	42
0	12	-100	-69
0	13	167	-128
1	0	-81	0
1	1	-85	-106
1	2	-103	-22
1	3	195	195
1	4	-102	32
1	5	166	-130
1	6	-111	33
1	7	91	38
1	8	-90	-87
1	9	108	5
1	10	-102	38
2	0	657	662
2	2	487	-505
2	3	-131	48
2	4	263	-277
2	5	153	-118
2	6	407	413
2	7	-87	87
2	8	379	377
2	9	264	293
2	10	560	-556
3	0	189	-199
3	1	163	150
3	2	142	148
3	3	89	-78
3	4	-74	-73
3	5	93	128
3	6	-91	75
3	7	149	-100
3	8	133	-58
3	9	-206	4
3	10	-92	3
4	0	201	-188
4	1	-102	-5
4	2	160	213
4	3	84	-37
4	3	-187	-37
4	4	692	-682
4	5	-142	-43
4	6	781	761
4	7	-91	-5
4	8	-93	63
4	9	93	141
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5	3	213	-187
5	4	-85	-2
5	5	237	246
5	6	-90	102
5	7	300	-297
5	8	-107	-39
6	0	-122	73
6	1	217	192
6	2	148	159
6	3	-85	3
6	4	569	-575
6	5	213	-193
6	6	622	641
6	7	-85	39
6	8	133	88
7	0	82	7
7	1	-87	-104
7	2	90	-154
7	3	238	275
7	4	150	184
7	5	220	-188
7	6	-92	-62
7	7	-94	64
8	1	195	-165
8	2	382	-379
8	3	186	141
8	4	-292	65
8	5	133	-145
8	6	-93	-23
9	0	128	-95
9	1	240	-248
9	3	343	325
9	4	-96	17
9	5	171	-162
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10	1	133	124
11	0	-100	-63
12	0	-357	7
		13	
1	0	131	169
1	1	590	-607
1	2	679	-657
1	3	190	-194
1	4	451	444
1	5	317	300
1	6	88	6
1	7	91	80
1	8	462	410
1	9	635	-603
1	10	436	-441
2	0	173	-231
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2	2	184	188
2	3	-97	36
2	4	145	-141
2	5	-85	-3
2	6	139	148
2	7	-88	-64
2	8	130	-127
2	9	-95	-41
2	10	113	139
3	0	581	-607
3	1	505	-517
3	2	184	179
3	3	235	-262
3	4	223	-195
3	5	681	663
3	6	427	434
3	7	-117	-38
3	8	160	-178
3	9	373	-364
4	0	-92	85
4	1	369	353
4	2	80	-102
4	3	-92	-143
4	4	-143	94
4	5	235	218
4	6	99	-92
4	7	268	-307
4	8	111	106
4	9	174	146
5	0	166	-276
5	1	-162	-18
5	2	208	192
5	3	399	-408
5	4	353	-336
5	5	661	662
5	6	449	464
5	8	159	-179
6	0	218	178
6	1	-86	81
6	2	161	-155
6	3	134	134
6	4	132	128
6	5	84	-7
6	6	-96	-101
6	7	98	-58
6	8	101	46
7	0	-92	-6
7	1	411	-422
7	2	133*	-82
7	3	153	-122
7	4	183	167
7	5	320	347
7	6	116*	-14
7	7	184	122
8	0	-109	-225
8	1	265	-225
8	2	234	227
8	3	460	419
8	4	164	-130
8	5	283	-267
9	0	252	232
9	1	494	-501
9	2	192	-195
9	3	-95	46
10	0	-102	-10
11	0	-105	-2
12	0	165	140
		14	
0	0	332	-341
0	1	505	-520
0	2	451	-446
0	3	707	686
0	4	1405	1402
0	5	455	-462
0	6	692	-667
0	7	396	410
0	8	-228	-6
0	9	662	-647
0	10	199	-218
0	11	306	311
0	12	412	394
0	13	-146	-33
1	0	165	-199
1	1	139	99
1	2	239	217
1	3	-92	-9
1	4	202	-225
1	5	-93	34
1	6	177	178
1	7	-91	-105
1	8	200	-169
1	9	118	91
2	0	730	-758
2	1	-98	-80
2	2	150	120
2	3	87	87
2	4	650	627
2	5	181	135
2	6	-85	53
2	7	-88	-193
2	8	501	-496
2	9	102	-172
3	0	-177	107
3	1	178	239
3	2	-85	-16
3	3	153	-130
3	4	-85	-9
3	5	47	164
3	6	-91	-115
3	7	129	-166
3	8	-95	74
3	9	-128	72
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4	2	492	487
4	3	483	-490
4	4	347	331
4	5	542	511
4	6	195	204
4	7	461	-481
4	8	674	-638
5	0	455	469
5	1	-92	79
5	2	303	-277
5	3	119	68
5	4	169	175
5	5	-93	7
5	6	305	-285
5	7	-126	-88
5	8	187	224
6	0	517	-505
6	1	84	38
6	2	121	-167
6	3	-90	41
6	4	631	625
6	5	91	-5
6	6	110	-165
6	7	-92	-7
7	0	88	-124
7	1	-90	-60
7	2	228	263
7	3	241	262
7	4	239	-271
7	5	223	-191
7	6	-95	111
8	0	554	-526
8	1	354	-348
8	2	123	-61
8	3	317	289
8	4	416	426
9	0	146	-98
9	1	-98	-12
10	0	424	-427
11	0	311	285
12	0	-115	-103
		15	
1	0	169	-201
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1	2	-94	95
1	3	1290	1305
1	4	225	194
1	5	1051	-995
1	6	-208	-2
1	7	97	111
1	8	248	-200
1	9	-107	-82
2	0	-98	99
2	1	370	367
2	2	-187	-4
2	3	366	-372
2	4	-93	-10
2	5	323	325
2	6	-86	-70
2	7	310	-239
2	8	-94	1
2	9	155	209
3	0	153	-126
3	1	1251	1202
3	2	130	-104
3	3	-193	-15
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3	5	176	177
3	6	-93	-103
3	7	944	-910
3	8	-91	-95
4	0	305	371
4	1	-96	-163
4	2	212	-185
4	3	-99	125
4	4	-106	83
4	5	-87	-125
4	6	262	-246
4	7	-97	91
4	8	288	226
5	0	182	-181
5	1	865	862
5	2	-145	23
5	3	268	268
5	4	89	81
5	5	233	-224
5	6	119	85
5	7	516	-516
6	0	100	118
6	1	151	-129
6	2	98	45
6	3	-92	66
6	4	164	-158
6	5	97	-112
6	6	100	-16
7	0	366	-329
7	1	130	67
7	2	161	144
7	3	777	737
7	4	-100	78
7	5	628	-638
8	0	185	-159
8	1	133	110
8	2	324	289
8	3	106	-115
9	0	-101	-0
10	0	219	215
11	0	-210	-61
		16	
0	0	156	31
0	1	150	-171
0	2	631	606
0	3	1008	986
0	4	1316	-1289
0	5	781	-772
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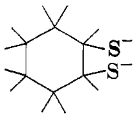
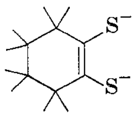
0	7	170	183
0	8	-114	80
0	9	399	-379
0	10	361	369
0	11	394	414
0	12	348	-356
1	0	212	198
1	1	181	208
1	3	210	-215
1	4	110	144
1	5	120	176
1	6	-105	-134
1	7	160	-164
1	7	226	-164
1	8	-97	113
2	0	1047	1079
2	1	224	244
2	2	298	-251
2	3	431	417
2	4	669	-648
2	5	99	-76
2	6	124	-81
2	7	367	-348
2	8	516	491
3	0	132	226
3	1	-110	-24
3	2	137	-184
3	3	109	-99
3	4	101	155
3	5	-89	48
3	6	221	-197
3	7	-316	31
4	0	1162	1168
4	1	774	779
4	2	407	-399
4	3	111	-99
4	4	241	-212
4	5	325	323
4	6	417	-411
4	7	537	-545
5	0	-101	31
5	1	269	-272
5	2	113	59
5	3	125	118
5	4	142	-120
5	5	188	-145
5	6	96	5
6	0	426	405
6	1	218	244
6	2	344	322
6	3	255	288
6	4	797	-778
6	5	171	-153
7	0	106	-40
7	1	162	82
7	2	201	135
7	3	203	-214
8	0	384	361
9	0	140*	3
10	0	488	498
11	0	-153	117
		17	
1	0	93	97
1	1	473	-464
1	2	572	-543
1	3	330	-333
1	4	913	-905
1	5	357	325
1	6	165	143
1	7	185	180
2	0	304	315
2	1	-92	-41
2	2	310	-340
2	3	-93	-37
2	4	343	335
2	5	-94	2
2	6	259	-273
2	7	-94	50
3	0	1079	1064
3	1	618	-619
3	2	457	-467
3	3	200	-187
3	4	-106	74
3	5	234	218
3	6	618	-599
4	0	-113	-67
4	1	167	-147
4	2	-96	72
4	3	-92	12
4	4	-301	-58
4	5	115	-66
4	6	-101	40
5	0	618	609
5	1	143	-97
5	2	95	-120
5	3	199*	-520
5	4	199	-231
5	5	484	502
6	0	-100	-108
6	1	-94	-43
6	2	-97	95
6	3	-114	-121
6	4	-186	-47
7	0	92	-91
7	1	106	-117
8	0	-104	-42
9	0	290	281
10	0	-112	-63
		18	
0	0	639	-649
0	1	105	80
0	2	554	536
0	3	643	-609
0	4	142	69
0	5	247	304
0	6	-94	-50
0	7	173	159
0	8	418	-432
0	9	158	139
0	10	344	376
1	0	-154	77
1	1	-95	-100
1	2	-198	-87
1	3	-107	81
1	4	-108	94
1	5	139	-85
1	6	-96	-63
2	0	280	-251
2	1	518	-500
2	2	140	177
2	3	197	-207
2	4	188	198
2	5	-111	84
2	6	-96	-122
3	0	-109	48
3	1	123	-132
3	2	-96	-105
3	3	-92	56
3	4	144	143
3	5	-156	-94
4	0	-97	-25
4	1	343	-403
4	2	201	-200
4	3	104	-123
4	4	535	543
4	5	-97	-54
5	0	135	-101
5	1	-95	-17
5	2	-283	15
5	3	-99	-54
6	0	171	-133
6	1	-96	85
7	0	113	-132
8	0	422	-437
9	0	-246	-93
		19	
1	0	344	-338
1	1	324	331
1	2	-95	109
1	3	135	-133
1	4	-297	77
1	5	105	-137
2	0	-96	4
2	1	126	-93
2	2	107	-65
2	3	-86	90
2	4	-157	88
2	5	-131	-82
3	0	139	-187
3	1	-91	-31
3	2	83	35
3	3	206	194
3	4	149	139
4	0	-290	-35
4	1	99	-92
4	2	-101	-34
4	3	-110	97
5	0	107	93
6	0	113	-120
7	0	103	-65
8	0	-108	-55
9	0	312	-304
		20	
0	0	-315	-45
0	1	254	243
0	2	-138	15
0	3	116	-164
0	4	264	-282
0	5	-102	-59
0	6	265	270
0	7	156	-40
0	8	-165	98
0	9	276	264
1	0	-95	34
1	1	-115	39
1	2	127	-54
1	3	-98	-12
2	0	167	167
2	1	-94	22
2	2	-99	-108
3	0	-99	-40
4	0	220	222
5	0	-112	-140
6	0	277	235
7	0	-104	3
8	0	-102	151
		21	
1	0	141	-66
2	0	-102	53
3	0	-101	26
4	0	161	-173
5	0	-186	-80
6	0	-112	-40
7	0	127	58
		22	
0	0	303	-28
0	1	311	32
0	2	-99	-10
0	3	304	-29
0	4	473	494
0	5	333	330
0	6	176	-159
1	0	-180	-13
2	0	334	-366
3	0	-110	-72
4	0	455	-463
5	0	114	-13
6	0	238	-269
		23	
1	0	-238	-5
2	0	171	-188
3	0	400	-423
4	0	155	100
		24	
0	0	558	554
0	1	161	81
0	2	264	-267
0	3	388	-159
1	0	144	-148
2	0	311	284
		26	
0	0	135	554

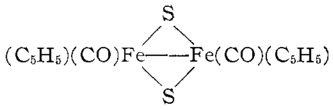
[a] Each group of four columns contains k, l, $10F_o$, and $10F_c$, respectively, and is headed by the value of h common to the group. Negative figures in the F_o column are threshold values for unobserved reflections. An asterisk following F_o indicates that the reflection was omitted from the final refinement cycles.

The appearance of absorptions in the aliphatic carbon–hydrogen stretching region in $(C_5H_5MoS_2C_6H_{11})_n$ supports the presence of a cyclohexylmercaptide group, and this compound may be a mixed sulfide–mercaptide complex. The data do not, however, rule out the possibility of the molybdenum complex being a derivative of the cyclohexane-1,2-dithiolate anion (**1**) or the cyclohexene-1,2-dithiolate anion (**2**), which would have the formulas $[C_5H_5Mo(S_2C_6H_{10})]_n$ and $[C_5H_5Mo(S_2C_6H_8)]_n$, respectively.


1


2

The intermediate compound in the preparation of $(C_5H_5FeS)_4$ is speculatively assigned the composition $[C_5H_5FeS(CO)]_2$ on the basis of the infrared spectrum and the structure of the final product $(C_5H_5FeS)_4$. If structure **3** is assumed for this intermediate, a displacement of CO by unshared pairs of electrons on the sulfur atoms of another molecule could lead to the formation of the tetrameric $(C_5H_5FeS)_4$.


3

Molecular Structure.—As shown in Figure 2, $(C_5H_5FeS)_4$ consists of an elongated tetrahedron of iron atoms with a sulfur atom over each face and a cyclopentadienyl group projecting from each corner. The exact molecular symmetry is m (C_s); considering the cyclopentadienyl groups as point substituents, the molecule has approximate symmetry $\bar{4}2m$ (D_{2d}). The two short edges of the iron tetrahedron are interiron bonds whose lengths of 2.618 ± 0.002 and 2.644 ± 0.002 A differ by a small but experimentally significant amount, possibly because of crystalline forces. The long edges of the iron tetrahedron are 3.368 ± 0.002 and 3.365 ± 0.002 A in length and are not interiron bonds. The Fe–S bonds fall into two classes, those paralleling the long axis of the tetrahedron averaging 2.256 ± 0.003 A in length and those bridging the interiron bonds averaging 2.206 ± 0.002 A in length. No S–S bonds are present; the shortest S–S distances are S(4)–S(6) and S(5)–S(6) at 2.883 ± 0.003 and 2.885 ± 0.003 A, respectively.

Table V

Comparison of Bond Lengths

Compound	Fe–Fe distance, A	Fe–S, distance, A	Ref
$(C_5H_5FeS)_4$	2.618 ± 0.002	2.206 ± 0.002[a]	This
	2.644 ± 0.002	2.256 ± 0.003[a]	work
$Fe_2(CO)_9$	2.46	...	18
$[C_5H_5Fe(CO)_2]_2$	2.49 ± 0.02	...	19
$[SFe(CO)_3]_2$	2.552 ± 0.002	2.228 ± 0.003[a]	16
	2.55 ± 0.01	2.216 ± 0.009[a]	20
$S_2Fe_3(CO)_9$	2.596 ± 0.008[a]	2.229 ± 0.006[a]	20
$CsFe_4S_3(NO)_7 \cdot H_2O$	2.71 ± 0.01[a]	2.20 ± 0.02[a,b]	
		2.25 ± 0.01[a,c]	21
$[C_2H_5SFe(NO)_2]_2$	2.72 ± 0.01	2.27	22

[a] This value represents an average distance for similar bonds. [b] This value represents the S–apical Fe bond distance. [c] This value represents the S–basal Fe bond distance.

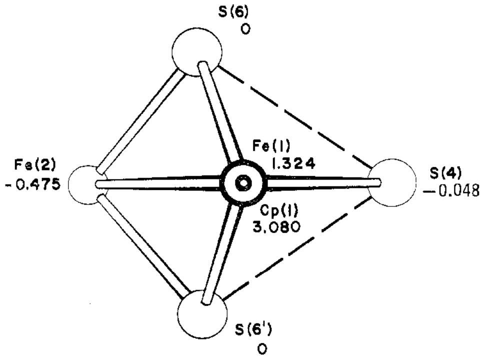


Figure 3.—Coordination about one of the iron atoms in $(C_5H_5FeS)_4$. The view is along the Cp(1)–Fe(1) axis; distances refer to heights above an arbitrary plane.

A summary of Fe–Fe and Fe–S bond lengths in related compounds is given in Table V.[18-22] The average interiron bond length of 2.631 A in $(C_5H_5FeS)_4$ is greater than those found in the carbon-bridged complexes but lies in the center of the range found for sulfur-bridged interiron bonds. The rather wide variation in iron–iron distances probably represents simply different hybrid character of the orbitals used in forming the interiron bond.[23] The Fe–S distances found in $(C_5H_5FeS)_4$ are very similar to those found in the other iron–sulfur complexes.

The average Fe–Cp (ring center) distance of 1.757 ± 0.005 A is somewhat longer than the values of 1.62 ± 0.02[24] and 1.66 ± 0.02 A[25] found in ferrocene by electron and X-ray diffraction, respectively. The longer value found here nonetheless agrees very well with that of 1.75 ± 0.03 A found in $[C_5H_5Fe(CO)_2]_2$.[19] The average C–C bond length in the cyclopentadienyl rings is 1.43 ± 0.01 A, in excellent agreement with an identical value found in ruthenocene,[26] where rigid molecular packing made librational corrections unnecessary, and with a librationally corrected estimate of 1.42 ± 0.03 A in $C_5H_5Mn(CO)_3$.[27]

Assuming each cyclopentadienyl ring occupies three coordination positions, each iron atom is seven-coordinate. A view along the Cp(1)–Fe(1) axis of the iron and sulfur atoms bonded to Fe(1) is given in Figure 3. This projection of bonded atoms is similar to that observed about the unique iron atom in $S_2Fe_3(CO)_9$[20] and the metal atoms in $[C_5H_5Mo(CO)_3]_2$,[28] C_5H_5Nb-

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$(CO)_4$,[28] and $[(C_5H_5)_2Mo_2H\{P(CH_3)_2\}(CO)_4]$.[28] However, in the present case, constraints imposed by bonds between coordinated atoms, rather than the hybridization state of the iron atom, largely determine the coordination geometry.

A few additional polynucleates based on a tetrahedral arrangement of metal atoms are known. A symmetrical tetrahedral structure has been suggested for the compound $(C_5H_5FeCO)_4$[29] and confirmed by preliminary X-ray studies.[30] A similar structure of $\bar{4}3m$ (T_d) symmetry is likely for $(C_5H_5CrO)_4$.[31] Somewhat less directly comparable is a series of Cu(I) complexes studied by Wells and co-workers. Mann, Purdie, and Wells[32] and Wells[33] have shown that $[(C_2H_5)_3AsCuI]_4$, $[(C_2H_5)_3AsCuBr]_4$, and $[(C_2H_5)_3PCuI]_4$ are isomorphous and have determined the crystal structure of $[(C_2H_5)_3AsCuI]_4$. In contrast to the (approximate) D_{2d} symmetry of the iron complex, the copper polynucleate has symmetry T_d. It is composed of a regular tetrahedron of copper atoms with an iodine atom centered over each face and a triethylarsine ligand projecting from each corner. In this compound, the intercopper distance is 2.60 A; Cu–I and Cu–As distances are 2.66 and 2.50 A, respectively.

Evaluation of the Hindered-Rotor Model.—One result of this investigation is an evaluation of the usefulness of the Lipscomb–King hindered-rotor scattering expression. The excellent agreement between the average C–C bond length found with the use of this expression and that found in an accurately determined structure[26] where thermal parameters are small demonstrates quite well the value of this formulation. Although the final R of 6.9% is higher than that (5.8%) obtained with the usual thermal ellipsoids, the reduction in number of parameters from 163 to 81 because of the transition to the hindered-rotor model justifies this rise. Constraints placed upon the structural model by the hindered-rotor approximation made refinement of the disordered cyclopentadienyl group much more straightforward and objective than would have been possible using ten independent carbon atoms. It must also be observed here that the model was used in a rather incorrect manner in describing Cp(3). As Figure 1c shows, this ring clearly librates about some point near C(9) rather than about its center. The widely varying extent of thermal motion of cyclopentadienyl rings in different crystals and the known low barrier to rotation in the gaseous state show that thermal movement of these groups in the crystal is largely determined by intermolecular forces. There is thus no *a priori* reason to suppose the ring librates about its center. Indeed, intermolecular distances in orthorhombic $(C_5H_5FeS)_4$ are greatest between the half-molecule described in Table II and those related by the transformations $(^1/_2 + x, ^1/_2 - y, z)$ and $(^1/_2 + x, -^1/_2 - y, z)$; *i.e.*, between the upper two molecules in Figure 4, or in the immediate neighborhood of C(7). The average bond length in this most highly moving ring increased from 1.368 to 1.411 ± 0.006 A on going to the hindered-rotor model, compared with a change from 1.436 to 1.448 ± 0.005 A for Cp(1), which is more rigidly restrained.

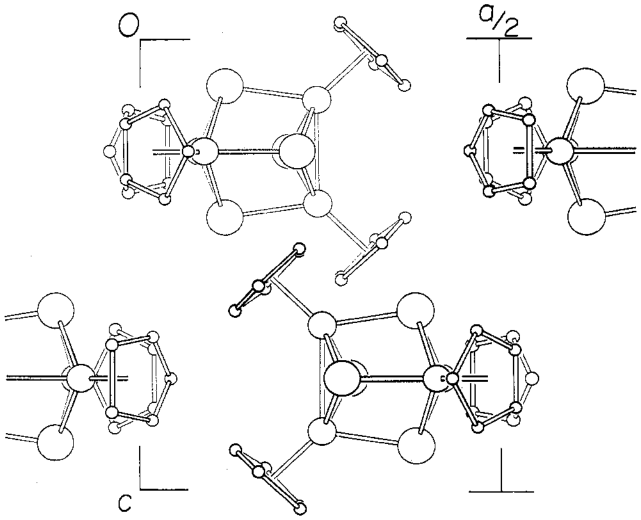

Figure 4.—Packing in orthorhombic $(C_5H_5FeS)_4$. See Figure 2 for labeling of the upper left-hand molecule. Lighter molecules are centered near $y = 0$, heavier ones near $y = ^1/_2$. Ring Cp(2) is shown in its predominant position only and is disordered with approximate frequencies 60–40% between the two positions allowed by the mirror.

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