

Crystallographic Studies on Sulfur Dioxide Insertion Compounds.

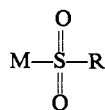
II. The Structure of a Sultine Derivative,

Melvyn R. Churchill*² and John Wormald

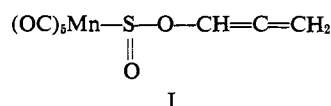
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Abstract: $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CCH}_3$ reacts with SO_2 to form the adduct $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_5\text{SO}_2$, the structure of which has now been determined by single-crystal X-ray diffraction studies. The complex crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ (C_{2h}^5 ; no. 14) with $a = 10.029 \pm 0.008$, $b = 7.353 \pm 0.006$, $c = 16.072 \pm 0.016$ Å, $\beta = 94.30 \pm 0.04^\circ$, $Z = 4$. Intensity data to $\sin \theta = 0.42$ (Mo $K\alpha$ radiation) were collected on a 0.01° -incrementing Supper-Pace Buerger automated diffractometer, the structure being solved by a combination of Patterson, Fourier, and least-squares refinement techniques. With all atoms (other than methyl hydrogens) located, the discrepancy index is $R_F = 5.80\%$ for the 1178 independent, nonzero reflections. The $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2$ portion of the molecule has the usual stereochemistry; however, the incoming SO_2 molecule does not insert into the iron-(σ -alkynyl) linkage, but rather, is involved in a sultine ring which is bonded to the iron atom *via* an iron-(σ -vinyl) linkage to form the system $\text{Fe}-\text{C}=\text{C}(\text{-CH}_3)-\text{S}(=\text{O})-\text{O}-\text{CH}_2$.

Wojcicki and coworkers have investigated SO_2 as an "insertion ligand"³ and have shown that it reacts with a transition metal alkyl or aryl (M-R) to produce the corresponding S-sulfinate⁴⁻¹⁰

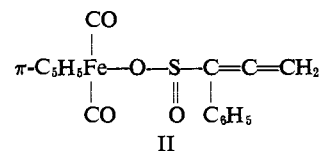


The reaction of $\text{Mn}(\text{CO})_5\text{CH}_2\text{C}\equiv\text{CR}$ or $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_5\text{CH}_2\text{C}\equiv\text{CR}$ with SO_2 yields a stable 1:1 adduct.¹¹⁻¹³ Infrared and proton magnetic resonance studies on the product from $\text{Mn}(\text{CO})_5\text{CH}_2\text{C}\equiv\text{CH}$ and SO_2 led to the suggestion that it was the allenyl(oxy)sulfanyl complex, I.



However, subsequent workers¹⁴ studied the reaction product from $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{-C}\equiv\text{CC}_6\text{H}_5$ and

SO_2 and proposed that it was the allenyl-O-sulfinate complex, II.



In order to ascertain unambiguously the nature of the product from SO_2 and a 2-alkynyl complex of a transition metal, we have carried out an X-ray crystallographic study on $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_5\text{SO}_2$ (prepared from $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CCH}_3$ and SO_2), and find it to have a structure containing a sultine ring (*vide infra*). A preliminary account of this work has appeared previously.¹⁵

Unit Cell and Space Group

A sample of the complex was supplied by Professor A. Wojcicki of The Ohio State University. Slow cooling of a 1:1 1,2-dichloroethane-methylcyclohexane solution yielded large yellow needle-shaped crystalline parallelepipeds which were air stable and not sensitive to irradiation by X-rays. Optical examination and the observed reciprocal lattice symmetry (C_{2h} ; $2/m$) indicated that the crystals belonged to the monoclinic system. Unit cell dimensions, obtained from precession photographs taken with Mo $K\alpha$ radiation (λ 0.7107 Å) at room temperature ($24 \pm 2^\circ$) and calibrated with lead nitrate ($a = 7.8566$ Å), are $a = 10.029 \pm 0.008$, $b = 7.353 \pm 0.006$, $c = 16.072 \pm 0.016$ Å, $\beta = 94.30 \pm 0.04^\circ$. The unit cell volume is 1182 Å³. Photographs of the levels $0-1kl$, $h0-1l$, $hk0-1$ revealed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, compatible only with space group $P2_1/c$ (C_{2h}^5 ; no. 14).¹⁶ The calculated density is 1.658 g cm⁻³ for $M = 294.11$ and $Z = 4$; the observed density is 1.6 ± 0.1 g cm⁻³ by flotation in aqueous zinc iodide solution (in which the

(1) Part I: M. R. Churchill and J. Wormald, *Inorg. Chem.*, **9**, 2430 (1970).

(2) Fellow of the Alfred P. Sloan Foundation, 1968-1970.

(3) While the term "insertion ligand" is convenient, it should not be regarded as indicative of reaction mechanism. Indeed, a reaction of the type $L_2\text{M}(\text{CO})\text{R} + \text{CO}^* \rightarrow L_2\text{M}(\text{CO}^*)(\text{COR})$ is known to occur *via* migration of R onto the already present CO ligand, rather than by insertion of the incoming CO^* into the M-R bond. See K. Noack and F. Calderazzo, *J. Organometal. Chem.*, **10**, 101 (1967).

(4) J. P. Bibler and A. Wojcicki, *J. Amer. Chem. Soc.*, **86**, 5051 (1964).

(5) F. A. Hartman and A. Wojcicki, *ibid.*, **88**, 844 (1966).

(6) J. P. Bibler and A. Wojcicki, *ibid.*, **88**, 4862 (1966).

(7) F. A. Hartman and A. Wojcicki, *Inorg. Chem.*, **7**, 1504 (1968).

(8) F. A. Hartman and A. Wojcicki, *Inorg. Chim. Acta*, **2**, 351 (1968).

(9) P. J. Pollick, J. P. Bibler, and A. Wojcicki, *J. Organometal. Chem.*, **16**, 201 (1969).

(10) M. Graziani, J. P. Bibler, R. M. Montesano, and A. Wojcicki, *ibid.*, **16**, 507 (1969).

(11) J. E. Thomasson and A. Wojcicki, *J. Amer. Chem. Soc.*, **90**, 2709 (1968).

(12) A. Wojcicki, J. J. Alexander, M. Graziani, J. E. Thomasson, and F. A. Hartman, Proceedings of the First International Inorganica Chimica Acta Symposium, Venice, Italy, 1968, Paper C-6.

(13) J. E. Thomasson, M. S. Thesis, Ohio State University, 1968.

(14) J.-L. Roustan and C. Charrier, *C. R. Acad. Sci., Ser. C*, **268**, 2113 (1969).

(15) M. R. Churchill, J. Wormald, D. A. Ross, J. E. Thomasson, and A. Wojcicki, *J. Amer. Chem. Soc.*, **92**, 1795 (1970).

(16) "International Tables for X-Ray Crystallography," Vol. I, The Kynoch Press, Birmingham, England, 1965, p 99.

crystals slowly dissolve). No crystallographic symmetry is imposed upon the molecule.

Collection and Reduction of the X-Ray Diffraction Data

The crystals used in the diffraction study were well-developed parallelepipeds of dimensions $0.08 \times 0.08 \times 0.29$ mm (*c* mounted) and $0.10 \times 0.07 \times 0.65$ mm (*b* mounted), dimensions in each case referring to the $10\bar{1}$, 100, and 010 directions (which are normal to the major crystal faces).

Intensity data were collected with Mo $K\alpha$ radiation (λ 0.7107 Å) on a 0.01° -incrementing Supper-Pace Buerger automated diffractometer, using a stationary-background, ω -scan, stationary-background counting technique and equininclination Weissenberg geometry.

While the apparatus and experimental technique have been described in full previously,¹⁷ details specific to the present analysis are: X-ray generator operated at 49 kV–19.6 mA; speed of ω scan = $2^\circ/\text{min}$; angle scanned (ω) = $[1.5 + (0.7/L)]^\circ$, where $1/L$ is the Lorentz factor; standard reflections measured after each 20 reflections, no significant (*i.e.*, $\geq 3(\text{count})^{1/2}$) variations from the mean being detected; initial and final backgrounds each counted for one-fourth the time of the ω scan.

Data for quadrants hkl and $\bar{h}kl$ of the levels $hk0$ – 6 were collected from the *c*-mounted crystal and data for similar quadrants of the levels $h0$ – $7l$ were collected from the *b*-mounted crystal. Within each level, data are complete to $\sin \theta = 0.42$, the limit of observable reflections on long-exposure Weissenberg photographs; no reflections in the range $0 < \theta \leq 4^\circ$ were collected, since these are shielded from the scintillation counter by a lead backstop.

Subsequent discussion necessitates the definition of the following symbols: C = count associated with ω scan, B_1 = initial background count, B_2 = final background count, t_C = time taken for ω scan, t_B = time taken for each background count. The integrated intensity of a reflection (I) is then given by

$$I = C - [0.5(t_C/t_B)(B_1 + B_2)]$$

Similarly, δ , the maximum probable error (*i.e.*, 3σ level) in the intensity of a reflection based solely on counting statistics, is given by

$$\delta = 3[C + 0.25(t_C/t_B)^2(B_1 + B_2)]^{1/2}$$

Based on previous experience with Mo $K\alpha$ radiation (as obtained by passing molybdenum radiation through a 3.0-mil zirconium filter) used in conjunction with the ω -scan technique, standard deviations were assigned to reflections on the basis

$$\begin{aligned} I \geq 4900 & \quad \sigma(I) = 0.1I \\ 4900 > I \geq \delta & \quad \sigma(I) = 7.0I^{1/2} \\ I < \delta & \quad \sigma(I) = -1.0 \end{aligned}$$

(This last condition simply rejects reflections which are not significantly above background at the 3σ level.) Of 964 reflections collected from the *c*-mounted crystal, 501 were rejected as not significantly above background; 580 of the 1814 reflections from the *b*-mounted crystal were similarly rejected. Intensities were corrected for Lorentz, polarization, and absorption effects¹⁸ ($\mu =$

(17) M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, **7**, 1123 (1968).

14.69 cm^{-1} for Mo $K\alpha$ radiation); transmission factors ranged from 0.715 to 0.939 (*c*-mounted crystal, volume $1.3 \times 10^{-6} \text{ cm}^3$) and 0.824 to 0.923 (*b*-mounted crystal, volume $5.2 \times 10^{-6} \text{ cm}^3$).

Symmetry-equivalent reflections within a zone were averaged and all data were merged to a common scale by a least-squares procedure which minimized a set of residuals linear in the logarithms of the individual scale factors.¹⁹ The resulting 1178 independent non-zero reflections were placed on an (approximately) absolute scale by means of a Wilson plot.²⁰ This and all subsequent processes were performed under the CRYRM or CRYM systems.²¹

Elucidation and Refinement of the Structure

A systematic survey of a three-dimensional Patterson map, which had been sharpened such that the average intensity was no longer θ dependent, revealed features consistent with an iron atom at 0.3075, -0.1725 , -0.1030 and a sulfur atom at 0.1465, 0.1960, 0.1360. A difference Fourier synthesis, phased only by iron and sulfur atoms ($R_F = 39.0\%$),²² revealed all the other nonhydrogen atoms. Four cycles of full-matrix refinement of positional and isotropic thermal parameters for the 17 nonhydrogen atoms led to convergence at $R_F = 9.32\%$, $R_{wF^2} = 5.29\%$. Hydrogen atoms (other than those of the methyl group) were now introduced in calculated positions (with C–H = 1.080 Å and the appropriate idealized geometry) and assigned thermal parameters, $B_H = 4.0 \text{ \AA}^2$; hydrogen parameters were held constant while positional and anisotropic thermal parameters of all nonhydrogen atoms were subjected to two cycles of full-matrix refinement. Two such sequences, with a final repositioning of hydrogen atoms, led to convergence at $R_F = 5.80\%$, $R_{wF^2} = 2.13\%$, $(\Delta/\sigma)_{\text{max}} = 0.04$.

A structure factor calculation now excluding hydrogen atom contributions ($R_F = 6.37\%$, $R_{wF^2} = 2.67\%$) was used in phasing a difference Fourier map which revealed peaks 0.34–0.80 electron \AA^{-3} in height close to the calculated positions of the nonmethyl hydrogen atoms. There were no signs of any methyl hydrogens nor any other significant features on this map.

Hamilton R -factor ratio tests²³ justify both the use of anisotropic thermal parameters and the inclusion of hydrogen atoms at the 99.5% level of confidence. At the end of the analysis, the standard error in an observation of unit weight was 1.05.

Scattering factors²⁴ for neutral iron, sulfur, oxygen, carbon, and hydrogen were used. The values for iron were corrected for the real component of dispersion ($\Delta f' = +0.4$ electron). Throughout the analysis, reflections were weighted as $w = [\sigma\{F_o^2\}]^{-2}$, where

(18) Using IMBIBE, a FORTRAN IV program for the IBM 360 written by J. Wormald. This program uses the Gaussian quadrature numerical integration method to determine absorption corrections for crystals of essentially arbitrary shape; see C. W. Burnham, *Amer. Mineral.*, **51**, 159 (1966).

(19) Using DIFCOR, an IBM 7094 program by G. N. Reeke; see also A. D. Rae, *Acta Crystallogr.*, **19**, 683 (1965).

(20) A. J. C. Wilson, *Nature (London)*, **150**, 152 (1942).

(21) CRYRM is an integrated set of crystallographic routines for the IBM 7094 computer written by Dr. R. E. Marsh and coworkers at the California Institute of Technology. CRYM is an analogous set of crystallographic routines for the IBM 360 computer.

(22) Discrepancy indices used within the text are $R_F = \Sigma|F_o| - |F_c| / \Sigma|F_o|$, $R_{wF^2} = \Sigma w(|F_o|^2 - |F_c|^2) / \Sigma wF_o^4$.

(23) W. C. Hamilton, *Acta Crystallogr.*, **18**, 502 (1965).

(24) Reference 16, Vol. III, pp 202–207.

Table II. Final Atomic Coordinates (with esd's)^{a,b} and Vibration Ellipsoids^{c,d} for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_8\text{SO}_2$

Atom	x	y	z	$B_{\text{maj}}, \text{\AA}^2$	$B_{\text{med}}, \text{\AA}^2$	$B_{\text{min}}, \text{\AA}^2$
Fe	-0.30863 (13)	0.33379 (17)	0.60421 (8)	2.92	2.50	2.10
S	0.14549 (27)	0.28411 (34)	0.63296 (18)	4.25	3.76	2.48
O(1)	0.1027 (7)	0.4939 (9)	0.6152 (4)	5.50	4.63	2.55
O(2)	0.1809 (7)	0.2570 (11)	0.7232 (5)	6.98	5.02	2.77
O(3)	-0.3468 (9)	0.7038 (11)	0.5430 (6)	9.41	6.56	3.22
O(4)	-0.3097 (9)	0.1635 (13)	0.4414 (5)	11.21	6.20	2.06
C(1)	-0.0420 (10)	0.5214 (13)	0.6129 (6)	4.09	3.68	1.93
C(2)	-0.1092 (8)	0.3414 (11)	0.6084 (5)	2.68	2.29	1.75
C(3)	-0.0225 (9)	0.2075 (12)	0.6138 (6)	3.33	2.87	1.98
C(4)	-0.0383 (11)	0.0035 (13)	0.6134 (7)	4.68	4.10	2.72
C(5)	-0.2890 (12)	0.2439 (18)	0.7277 (6)	7.41	4.48	1.47
C(6)	-0.3644 (13)	0.3992 (17)	0.7237 (7)	8.09	4.07	2.06
C(7)	-0.4809 (11)	0.3644 (17)	0.6690 (7)	6.97	4.26	1.90
C(8)	-0.4738 (12)	0.1874 (16)	0.6408 (7)	6.76	4.45	2.13
C(9)	-0.3537 (13)	0.1094 (15)	0.6777 (8)	7.90	4.01	2.40
C(10)	-0.3252 (10)	0.5602 (17)	0.5659 (7)	5.53	4.67	1.82
C(11)	-0.3096 (11)	0.2279 (15)	0.5050 (7)	5.66	3.75	2.67
H(1)	-0.0786	0.6010	0.5586			
H(2)	-0.0626	0.5920	0.6685			
H(3)	-0.3396	0.5250	0.7561			
H(4)	-0.5611	0.4588	0.6521			
H(5)	-0.5471	0.1205	0.5984			
H(6)	-0.3191	-0.0276	0.6682			
H(7)	-0.1946	0.2279	0.7641			

^a Esd's are in parentheses after each parameter, right adjusted to the least significant digit of the preceding number. ^b Hydrogen atoms H(1) and H(2) are bonded to C(1); H(3)–H(7) are bonded to C(5)–C(9). ^c Major, median, and minor axes of the atomic vibration ellipsoid are defined in terms of the isotropic thermal parameter, B . The transformation to root-mean-square displacement is $(\bar{U}^2)^{1/2} = [B/8\pi^2]^{1/2}$. ^d The atomic vibration ellipsoids are illustrated in Figure 1.

$\sigma\{F_o^2\}$ is derived from $\sigma(I)$ by appropriate adjustment for Lorentz, polarization, absorption, and scale factors.

Structure factor amplitudes are displayed in Table I.²⁵

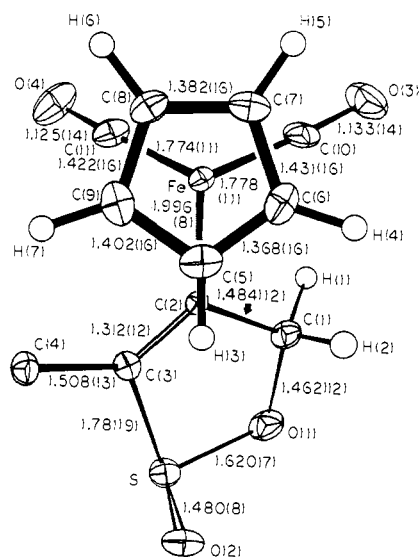


Figure 1. Thermal vibration ellipsoids, bond lengths, and labeling of atoms for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_8\text{SO}_2$.²⁶

The Molecular Structure

The molecular structure, with bond lengths, numbering scheme for atoms, and thermal vibration ellipsoids, is illustrated in Figure 1.²⁶ The coordination about the

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iron atom is shown in Figure 2. Atomic positions and thermal vibration ellipsoids are listed in Table II, anisotropic thermal parameters in Table III, and interatomic angles in Table IV.

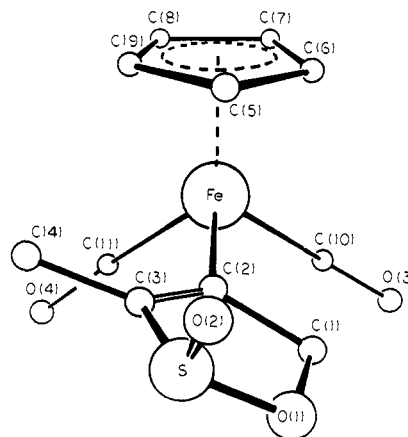


Figure 2. The $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_8\text{SO}_2$ molecule, showing the stereochemistry about the central iron atom and the conformation of the sultine ring.

As may be seen from Figures 1 and 2, the product from the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{C}\equiv\text{CCH}_3$ and SO_2 is neither an allenyl(oxy)sulfinyl nor an allenyl-*O*-sulfinate, but, rather, is a *sultine* (a cyclic ester of a sulfinic acid).²⁷ The molecule may be systematically named 3-methyl-4-(π -cyclopentadienyldicarbonyliron)-3,4-dehydro-1,2-oxathiolane 2-oxide.

(26) This diagram was constructed using OTLIPS, an IBM 1620-CALCOMP plotter program written by P. H. Bird.

(27) R. S. Henion, "Eastman Organic Chemistry Bulletin," Vol. 41, No. 3, 1969.

Table III. Anisotropic Thermal Parameters for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_5\text{SO}_2^{\text{a,b}}$ ($\times 10^4$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	55.2 (1.3)	130.1 (2.6)	24.2 (0.6)	-16.3 (3.8)	3.4 (1.3)	-5.8 (2.3)
S	65.5 (3.0)	173.0 (5.7)	40.8 (1.4)	-13.5 (6.6)	19.3 (3.2)	-0.8 (4.3)
O(1)	83 (9)	199 (16)	46 (4)	-78 (19)	-4 (9)	8 (13)
O(2)	88 (10)	314 (21)	42 (4)	37 (22)	-21 (9)	30 (15)
O(3)	144 (13)	233 (20)	80 (6)	82 (26)	-12 (13)	92 (18)
O(4)	181 (14)	426 (26)	30 (4)	-147 (31)	22 (11)	-113 (17)
C(1)	61 (12)	151 (20)	39 (5)	-54 (26)	13 (12)	-4 (16)
C(2)	57 (10)	93 (16)	23 (4)	-14 (24)	-5 (10)	-8 (14)
C(3)	75 (11)	134 (20)	23 (4)	4 (25)	24 (11)	6 (14)
C(4)	106 (14)	127 (20)	44 (6)	-13 (28)	18 (14)	-6 (17)
C(5)	108 (15)	341 (34)	17 (5)	-4 (38)	30 (13)	21 (24)
C(6)	117 (16)	262 (29)	41 (6)	-81 (36)	75 (16)	-77 (20)
C(7)	65 (12)	304 (32)	40 (6)	7 (34)	42 (13)	43 (21)
C(8)	95 (14)	242 (27)	42 (6)	-142 (36)	20 (14)	18 (22)
C(9)	141 (18)	180 (23)	50 (7)	1 (34)	94 (17)	28 (21)
C(10)	49 (12)	249 (27)	46 (6)	44 (30)	8 (13)	-4 (21)
C(11)	73 (13)	251 (28)	36 (5)	-54 (27)	13 (13)	-6 (18)

^a The anisotropic thermal parameter (T) is defined as $T = \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. ^b Esd's are shown in parentheses.

Table IV. Bond Angles within the $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{C}_4\text{H}_5\text{SO}_2$ Molecule^a

Atoms	Angle, deg	Atoms	Angle, deg
(a) Within Five-Membered Sultine Ring			
C(1)-C(2)-C(3)	111.7 (9.8)	S-O(1)-C(1)	112.6 (0.6)
C(2)-C(3)-S	112.8 (0.7)	O(1)-C(1)-C(2)	109.0 (0.8)
C(3)-S-O(1)	92.1 (0.4)		
(b) External Angles of the Sultine Ligand			
Fe-C(2)-C(1)	118.5 (0.6)	S-C(3)-C(4)	114.4 (0.7)
Fe-C(2)-C(3)	129.7 (0.7)	C(3)-S-O(2)	106.3 (0.4)
C(2)-C(3)-C(4)	132.6 (0.9)	O(1)-S-O(2)	109.9 (0.4)
(c) Associated with $\pi\text{-C}_5\text{H}_5$ Ligand			
C(5)-Fe-C(6)	38.2 (0.5)	C(5)-C(6)-C(7)	107.6 (1.1)
C(6)-Fe-C(7)	39.9 (0.5)	C(6)-C(7)-C(8)	108.1 (1.0)
C(7)-Fe-C(8)	38.5 (0.4)	C(7)-C(8)-C(9)	107.8 (1.0)
C(8)-Fe-C(9)	39.6 (0.5)	C(8)-C(9)-C(5)	107.2 (1.0)
C(9)-Fe-C(5)	39.2 (0.5)	C(9)-C(5)-C(6)	109.4 (1.1)
(d) In Carbonyl Ligands			
Fe-C(10)-O(3)	174.2 (1.0)	Fe-C(11)-O(4)	178.8 (1.0)
(e) Around Iron Atom ^b			
C(2)-Fe-C(10)	93.0 (0.4)	C(2)-Fe-Cp	121.9 (0.5)
C(2)-Fe-C(11)	88.9 (0.4)	C(10)-Fe-Cp	121.5 (0.5)
C(10)-Fe-C(11)	96.1 (0.5)	C(11)-Fe-Cp	126.5 (0.5)

^a Esd's, shown in parentheses, are right adjusted to the least significant digit of the preceding number. ^b Cp is the center of gravity of the π -cyclopentadienyl ligand.

The central Fe(II) atom has a d^6 electronic configuration and attains the appropriate noble gas configuration by the donation of six electrons from a π -cyclopentadienyl anion, two electrons from each of the two terminal carbonyl ligands, and two electrons from the substituted σ -vinyl fragment, $\text{C}_4\text{H}_5\text{SO}_2$. Since the $\pi\text{-C}_5\text{H}_5$ ligand is customarily regarded as a tridentate ligand, the Fe(II) ion is pseudooctahedrally coordinated (see Figure 2). Angles between the three monodentate ligands—C(2)-Fe-C(10) = 93.0 (0.4), C(2)-Fe-C(11) = 88.9 (0.4), C(10)-Fe-C(11) = 96.1 (0.5)^o—are consistent with this view.

As shown clearly in Figure 1, the three monodentate ligands adopt the most symmetrical possible conformation relative to the π -cyclopentadienyl ring. Thus, the substituted σ -vinyl ligand passes directly below C(5) while the carbonyl groups C(10)-O(3) and C(11)-O(4) pass beneath the C(6)-C(7) and C(8)-C(9) bonds,

respectively. The Fe(II) ion is therefore in a local environment which approximates to C_s symmetry. Angles involving Cp (the center of gravity of the π -cyclopentadienyl ring) are Cp-Fe-C(2) = 121.9 (0.5), Cp-Fe-C(10) = 121.5 (0.5), and Cp-Fe-C(11) = 126.5 (0.5)^o.

The Sultine Ligand

The sultine ring is formed by the insertion of SO_2 into the but-2-ynyl group of $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{-C}\equiv\text{CCH}_3$, which is accompanied by migration of the iron atom from C(1) to C(2) of the four-membered carbon chain.

The Fe-C(2) linkage is 1.996 (8) Å in length, in excellent agreement with the previously measured iron-(σ -vinyl) bond distances of 1.987 (5) Å in ($\pi\text{-C}_5\text{H}_5$) $\text{Fe}(\text{CO})_2\text{CH}=\text{CH}-\text{CH}=\text{CHF}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$,²⁸ and 1.99 (2) Å in ($\text{C}_5\text{H}_5\text{C}_2\text{CO}_2\text{CH}_2$) $\text{Fe}(\text{CO})_3$.²⁹ Each of these values is significantly shorter than an iron-carbon σ bond of unit bond order (*cf.* 2.11 (2) Å for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{-}\sigma\text{-C}_5\text{H}_5$,^{30a} 2.06 (2) Å for $\pi\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CH}_2\text{-CO}_2\text{H}$ ^{30b}) even after allowing for the difference of approximately 0.03 Å in the covalent radii of sp^2 - and sp^3 -hybridized carbon atoms. This may be taken as indicative of partial multiple-bond character in the iron-(σ -vinyl) linkage.³¹

Carbon-carbon bond lengths within the sultine system are: C(1)-C(2) = 1.484 (12) and C(3)-C(4) = 1.508 (13) Å (each compatible with the accepted $\text{C}(sp^2)\text{-C}(sp^3)$ single-bond distance of 1.510 ± 0.005 Å³²) and C(2)-C(3) = 1.312 (12) Å, which is close to the recognized $\text{C}=\text{C}$ distance of 1.335 ± 0.005 Å.³² The distances C(1)-O(1) = 1.462 (12), S-O(1) = 1.620 (7), and S-C(3) = 1.781 (9) Å are consistent with normal single bonds, while the S-O(2) distance of 1.480 (8) Å is indicative of a S=O double bond.³² Angles about

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(29) L. F. Dahl, R. J. Doedens, W. Hübel, and J. Nielsen, *J. Amer. Chem. Soc.*, **88**, 446 (1966).

(30) (a) M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lipard, and S. M. Morehouse, *ibid.*, **88**, 4371 (1966); (b) J. K. P. Ariyaratne, A. M. Bjerrum, M. L. H. Green, M. Ishaq, C. K. Prout, and M. G. Swantck, *J. Chem. Soc. A*, 1309 (1969).

(31) M. R. Churchill, "Perspectives in Structural Chemistry," Vol. 3, J. D. Dunitz and J. A. Ibers, Ed., Wiley, New York, N. Y., 1970, pp 128-133, 154.

(32) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, No. 18, 10 (1965).

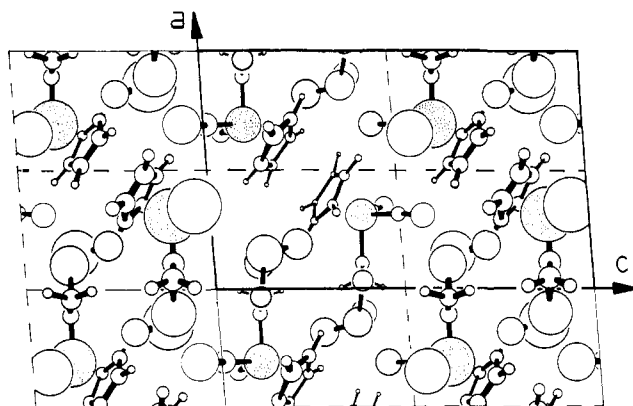


Figure 3. Packing of molecules in the crystal, projected on 010.

the sulfur atom, $O(1)-S-O(2) = 109.9(0.4)$, $O(1)-S-C(3) = 106.3(0.4)$, and $O(2)-S-C(3) = 92.1(0.4)^\circ$ indicate tetrahedral hybridization of the S(IV) valence orbitals, requiring a sterically active lone pair.

Each of the atoms Fe, C(1), C(2), C(3), and C(4) deviates by less than 0.03 \AA from their least-squares plane, $-0.0527X + 0.0039Y + 0.9918Z - 9.8730 = 0^{33}$ (see Table V). The atom O(1) lies essentially in this plane (deviation = -0.028 \AA), but the other atoms of the system are displaced toward the π -cyclopentadienyl ring, their deviations from the specified plane being $+0.228 \text{ \AA}$ for S and $+1.659 \text{ \AA}$ for O(2).

Table V. Least-Squares Planes within the $\pi-C_5H_5Fe(CO)_2C_4H_5SO_2$ Molecule^{a,b}

Atom	Distance, \AA	Atom	Distance, \AA
(A)	$-0.0527X + 0.0039Y + 0.9918Z - 9.8730 = 0$		
Fe*	+0.008	C(4)*	+0.003
C(1)*	+0.011	O(1)	-0.028
C(2)*	-0.029	O(2)	+1.659
C(3)*	+0.007	S	+0.228
(B)	$-0.5456X - 0.3121Y + 0.7777Z - 10.5758 = 0$		
C(5)*	-0.003	C(8)*	-0.003
C(6)*	+0.001	C(9)*	+0.004
C(7)*	+0.001	Fe	-1.722

^a All planes are expressed in Cartesian coordinates: $X = xa + zc \cos \beta$, $Y = yb$, $Z = zc \sin \beta$. ^b Planes are derived using unit weights for atoms marked with asterisks, zero weights for others.

Internal angles of the sultine ring are $C(1)-C(2)-C(3) = 111.7(0.8)$, $C(2)-C(3)-S = 112.8(0.7)$, $C(3)-S-O(1) = 106.3(0.4)$, $S-O(1)-C(1) = 112.6(0.6)$, and $O(1)-C(1)-C(2) = 109.0(0.8)^\circ$. The contraction of the internal angles at C(2) and C(3) by about 8° (relative to the ideal sp^2 value of 120°) appears to represent the most strained feature of this five-membered heterocyclic system.

The reason for the large exocyclic bond angles $Fe-C(2)-C(3) = 129.7(0.7)$ and $C(2)-C(3)-C(4) = 132.6(0.9)^\circ$ may be partially electronic, but there is some steric interaction between the C(4) methyl group and methylene hydrogens [H(1) and H(2)] on the symmetry-related molecule at $x, 1 + y, z$ (see Table VI).

The π -Cyclopentadienyl Ligand

As shown in Table V, the five carbon atoms of the π -cyclopentadienyl ring have a mean deviation of only

(33) Cartesian coordinates (see Table V).

Table VI. Intermolecular Contacts (to 3.5 \AA) in the $\pi-C_5H_5Fe(CO)_2C_4H_5SO_2$ Crystal

Atoms ^a	Distance, \AA	Atoms	Distance, \AA
S...H(4), I	3.20	H(1)...C(4), II	3.11
S...H(5), I	3.39	H(2)...C(4), II	3.17
O(1)...H(4), I	3.39	H(3)...O(4), V	3.28
O(2)...H(4), I	3.26	H(4)...S, VI	3.20
O(3)...H(6), II	2.82	H(4)...O(1), VI	3.39
O(4)...H(3), III	3.28	H(4)...O(2), VI	3.26
O(4)...H(7), III	3.25	H(5)...S, VI	3.39
C(4)...H(1), IV	3.11	H(6)...O(3), IV	2.82
C(4)...H(2), IV	3.17	H(6)...C(10), IV	3.45
C(10)...H(6), II	3.45	H(7)...O(4), V	3.25

^a Translations are: I, = $1 + x, y, z$; II = $x, 1 + y, z$; III = $x, 1/2 - y, -1/2 + z$; IV = $x, -1 + y, z$; V = $x, 1/2 - y, 1/2 + z$; VI = $-1 + x, y, z$.

0.003 \AA from their least-squares plane. The iron atom lies 1.722 \AA below this plane, the iron-carbon distances being $Fe-C(5) = 2.086(11)$, $Fe-C(6) = 2.096(12)$, $Fe-C(7) = 2.095(11)$, $Fe-C(8) = 2.096(11)$, and $Fe-C(9) = 2.097(11) \text{ \AA}$. The mean Fe-C (cyclopentadienyl) distance is $2.094 \pm 0.011 \text{ \AA}$. Carbon-carbon distances range from $1.368(16)$ to $1.431(16) \text{ \AA}$, averaging $1.401 \pm 0.024 \text{ \AA}$ —not appreciably lower than the value of $1.431(5) \text{ \AA}$ obtained by electron diffraction studies on ferrocene.^{34,35}

The Carbonyl Ligands

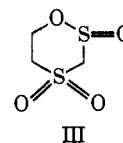
The mean Fe-CO and C-O bond lengths of $1.776(11)$ and $1.129(14) \text{ \AA}$ and the average Fe-C-O angle of $176.5(2.3)^\circ$ are consistent with values obtained previously from molecules containing a $\pi-C_5H_5Fe(CO)_2$ group.²⁸

The Crystal Structure

Figure 3 shows the arrangement of molecules within the crystal, projected onto 010. A list of intermolecular contacts (to 3.5 \AA) is given in Table VI. The molecules are separated by normal van der Waals' distances, the closest contact being $O(3)...H(6) = 2.82 \text{ \AA}$. One should note, however, that each of the contacts $C(4)...H(1)$ 3.11 \AA and $C(4)...H(2)$ 3.17 \AA involves C(4), the methyl carbon, whose hydrogen atoms were not located in this analysis. Contacts involving the methyl hydrogens and H(1), IV or H(2), IV are expected to be significantly shorter.

Discussion

While the sultine 1,2,4-oxadithiane 2,4,4-trioxide (III) was prepared in 1893,³⁶ it was not until 1967 that



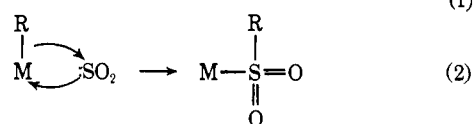
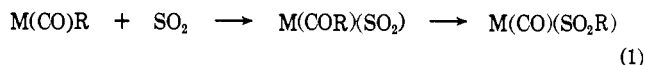
(34) R. K. Bohn and A. Haaland, *J. Organometal. Chem.*, **5**, 470 (1966).

(35) However, Figure 1 of this manuscript shows the thermal parameters of C(5)-C(9) to be consistent with libration of the π -cyclopentadienyl ligand about its C_5 symmetry axis. The present analysis is therefore expected to show C-C bond lengths which are systematically decreased from the true C-C (π -cyclopentadienyl) distance of $\sim 1.43 \text{ \AA}$.

(36) E. Baumann and G. Walter, *Ber.*, **26**, 1124 (1893).

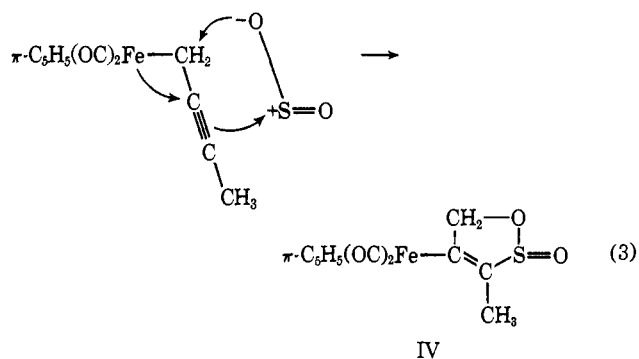
another example of a cyclic ester of a sulfinic acid was reported.³⁷ Furthermore, not one of the known sultines³⁸ has been synthesized directly from SO₂. It is therefore of some interest to consider some of the insertion reactions³ of SO₂ with transition metal carbonyl derivatives.

While the reaction of such transition metal carbonyl derivatives as Mn(CO)₅R,^{5,7,8} Re(CO)₅R,⁷ π-C₅H₅Fe(CO)₂R,^{4,6} π-C₅H₅Mo(CO)₃R,¹⁰ or π-C₅H₅W(CO)₃R¹⁰ (R = alkyl or aryl) with sulfur dioxide is known to give rise to S-sulfonates, the mechanism of this reaction has not been elucidated. Possibilities include attack of SO₂ on the metal atom (M) accompanied by the formation of an intermediate acyl derivative (eq 1) or attack of SO₂ on the metal in concert with alkyl migration onto the incoming SO₂ molecule, a kind of oxidative addition reaction of sulfur (eq 2).

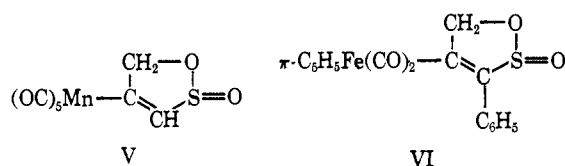


It is difficult, however, to envisage how the present sultine complex, π-C₅H₅Fe(CO)₂C₄H₉SO₂ (IV), can be formed *via direct attack* of SO₂ on the iron atom. Rather, the formation of the sultine ring and the concomitant migration of the iron atom from C(1) to C(2) are more simply explained *via* some concerted mechanism such as that shown in eq 3.

(37) R. S. Henion, Ph.D. Thesis, Syracuse University, 1967; D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969).
 (38) The chemistry of sultines has been reviewed; see ref 27.



Finally, it should be noted that the properties of Mn(CO)₅C₃H₃SO₂ (previously¹¹⁻¹³ assigned structure I) and π-C₅H₅Fe(CO)₂C₃H₂(C₆H₅)SO₂ (previously¹⁴ assigned structure II) are consistent with these species being reformulated as the sultine derivatives V and VI, respectively.



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