alternate configurations for the hydrogen. The lack of a satisfactory unique hydrogen-bond configuration may contribute to the ease with which water can escape from the structure.

It is a common practice to identify a phase by its ideal composition when variable composition exists, and we refer to this crystalline phase as the octahydrate because that would be the composition if all the water sites were occupied.

Registry No. $\text{Fe(C}_{12}\text{N}_2\text{H}_8)_3(\text{C}_4\text{O}_6\text{H}_2\text{Sb})_2\cdot 8\text{H}_2\text{O}$, 40354-54-9.

Acknowledgment. We thank Professor Richard E. Powell for bringing this problem to our attention and providing us with crystals.

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Crystallographic Studies on Sulfur Dioxide Insertion Compounds. IV. Structure of μ-(Sulfur dioxide)-bis(π-cyclopentadienyldicarbonyliron), Including the Location and Refinement of Hydrogen Atoms

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The species μ-(sulfur dioxide)-bis(π-cyclopentadienyldicarbonyliron), $[\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2\text{SO}_2$, crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}{}^5$; No. 14) with $a = 7.7028$ (17), $b = 17.1559$ (45), $c = 12.8488$ (27) Å; $\beta = 117.48$ (1)°; $Z = 4$. X-Ray diffraction data, complete to $2\theta = 55°$ (Mo Kα radiation), were collected with a Picker FACS-1 diffractometer, and the structure was solved by means of Patterson and Fourier syntheses. All atoms, including hydrogens, have been located; convergence of the least-squares refinement process occurred with $R_F = 3.01\%$ and $R_{wF} = 3.63\%$ for the 3472 independent reflections. The SO_2 moiety is "inserted" symmetrically between two iron atoms, with Fe(1)-S = 2.2790 (6) Å and Fe(2)-S = 2.2814 (7) Å. Sulfur-oxygen distances are S-O(1) = 1.4797 (15) Å and S-O(2) = 1.4764 (14) Å.

Introduction

The "insertion"[1] of sulfur dioxide into transition metal-carbon bonds has been studied in detail, principally by Wojcicki and his coworkers.[2] We have previously determined the crystal and molecular structures of diverse products of this class of reaction, *viz.*, $\text{C}_4\text{H}_6\text{Fe(CO)}_3\cdot\text{SO}_2\cdot\text{BF}_3$,[3] $\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{C}_4\text{H}_5\text{SO}_2$,[4] and $[\pi\text{-C}_5(\text{CH}_3)_5]\text{Fe(CO)}_2\text{SO}_2\text{-CH}_2\text{CH=CHC}_6\text{H}_5$,[5] and are now extending our studies to species in which an SO_2 molecule is inserted into a metal-metal bond. The present article concerns the structure of $[\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2\text{SO}_2$ which is formed by the reaction of $\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2\text{Na}$ and SO_2 in tetrahydrofuran.[6] $[\pi\text{-C}_5\text{H}_5\text{-Fe(CO)}_2]_2\text{SO}_2$ represents the first example of a neutral molecule in which two transition metal atoms are linked together solely by means of an SO_2 "bridge." It should be noted, however, that certain ionic species, *e.g.*, $[(\text{NC})_5\text{Co-(SO}_2)\text{Co(CN)}_5{}^{6-}]$[7] and $[(\text{OC})_5\text{M(SO}_2)\text{M(CO)}_5{}^{2-}]$ (M = Cr, W),[8] have previously been synthesized. Examples of Sn-(SO_2)-Sn and Fe-(SO_2)-Sn systems have also been documented.[9]

Collection and Correction of the X-Ray Diffraction Data

Red crystals of $[\pi\text{-C}_5\text{H}_5\text{Fe(CO)}_2]_2\text{SO}_2$ were provided by Professor A. Wojcicki of the Ohio State University. A preliminary survey of $h(0\text{-}2)l$ and $(0\text{-}2)kl$ precession photographs, together with a and b cone-axis photographs, yielded approximate cell dimensions, indicated C_{2h} $(2/m)$ Laue symmetry, and showed the systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$, consistent only with the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}{}^5$; No. 14).

The crystal used for data collection had an approximately rectangular cross section with the bounding faces being (100), $(\bar{1}00)$, $(0\bar{1}0)$, and a slightly damaged and rounded (010) face which approximated in orientation to the (1,17.6,0) plane. [Dimensions were (100) → $(\bar{1}00)$ = 0.41 mm and $(0\bar{1}0)$ → "(1,17.6,0)" = 0.23 mm.] The crystal was 0.42 mm in length with one end truncated by $(1\bar{1}\bar{1})$ and $(\bar{2}\bar{1}\bar{7})$ and the other end truncated by $(\bar{1}11)$, $(\bar{1}\bar{1}1)$, and $(0\bar{2}1)$.

The crystal was accurately centered on a Picker FACS-1 diffractometer and was orientated such that its $\bar{1}04$ axis was coincident with the instrumental ϕ axis.

Unit cell dimensions, determined from the 2θ, ω, and χ settings of the resolved Mo Kα_1 ($\lambda = 0.70926$ Å) peaks of 12 high-angle reflections ($2\theta = 37\text{-}52°$), measured under "high resolution" conditions[10] at 26° are $a = 7.7028$ (17), $b = 17.1559$ (45), $c = 12.8488$ (27) Å; and $\beta = 117.48$ (1)°. The unit cell volume is 1506.5 Å^3, yielding a calculated density of 1.844 g cm^{-3} for $M = 417.99$ and $Z = 4$. (The density was not measured experimentally due to an insufficient quantity of sample.)

Intensity data were collected[10] using Mo Kα radiation (*i.e.*, molybdenum radiation filtered through niobium foil) by executing a coupled θ-2θ (crystal-counter) scan from 1.0° in 2θ below the Kα_1 peak to 1.0° in 2θ above the Kα_2 peak. Each scan was executed at 1.0 deg min^{-1}, accumulating P counts in t_P seconds. Stationary background counts, of 40-sec duration each, were recorded at the low and high 2θ limits of the scan, giving B_1 and B_2 counts (respectively) for a total background counting time of t_B = 80 sec. Copper foil attenuators, whose transmission factors for Mo Kα

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(1) The term "insertion" is here used to describe a situation whereby a species X interacts with an A-B bond to form an A-X-B moiety. No *mechanistic* connotations are implied.

(2) A. Wojcicki, *Accounts Chem. Res.*, 4, 344 (1971).

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

(4) Part II: M. R. Churchill and J. Wormald, *J. Amer. Chem. Soc.*, 93, 354 (1971).

(5) Part III: M. R. Churchill and J. Wormald, *Inorg. Chem.*, 10, 572 (1971).

(6) M. R. Churchill, B. G. DeBoer, K. L. Kalra, P. Reich-Rohrwig, and A. Wojcicki, *J. Chem. Soc., Chem. Commun.*, 981 (1972).

(7) A. A. Vlcek and F. Basolo, *Inorg. Chem.*, 5, 156 (1966).

(8) J. K. Ruff, *Inorg. Chem.*, 6, 2080 (1967).

(9) R. E. J. Bichler and H. C. Clark, *J. Organometal. Chem.*, 23, 427 (1970).

(10) Exhaustive details of the apparatus and experimental procedure have appeared previously: M. R. Churchill and B. G. DeBoer, *Inorg. Chem.*, 12, 525 (1973).

radiation had previously been accurately determined (and which reduced the diffracted beam by successive factors of ~3.0–3.5), were inserted as necessary to keep the maximum counting rate below ~8500 counts $\sec^{-1}$, thereby obviating any significant coincidence losses.

The take-off angle was 3.0° and the detector was 330 mm from the crystal with an aperture of 6 × 6 mm.

Before collecting intensity data, a strong axial reflection, $\bar{2}08$, was measured by a θ-2θ scan at $\chi = 90°$ and from $\phi = 0°$ to $\phi = 350°$ at intervals of 10°. The variation in intensity was 31%, indicating that an absorption correction was mandatory. (These data were processed with the principal data set, *vide infra*. After correction for absorption the variation of intensity with ϕ was reduced to 2.8%.)

All reflections of the type hkl and $\bar{h}kl$ in the range $0° < 2\theta < 55°$ were measured. These included 3472 Laue-independent reflections, 146 $\bar{h}k0$ reflections, and 128 systematically absent reflections (each of which was found to confirm the extinction conditions for space group $P2_1/c$). Three strong "check reflections" (400; 0,12,8; $20\bar{8}$) were measured after each batch of 48 reflections in order to monitor crystal decomposition or possible changes in orientation. No change in orientation was detectable. The three check reflections had root-mean-square deviations in intensity of 0.87, 1.32, and 0.91%, respectively. These deviations were reduced to 0.44, 1.04, and 0.44% by assuming a linear decay throughout the data-collection process.

The integrated intensity, I, and its estimated standard deviation, $\sigma(I)$, were calculated from the expressions

$$I = q[(P + 4.5) - (t_P/t_B)(B_1 + B_2 + 9.0)]$$

and

$$\sigma(I) = q[(P + 4.5) + (t_P/t_B)^2(B_1 + B_2 + 9.0) + 24.75 + q^{-2}p^2I^2]^{1/2}$$

The "ignorance factor" (p) was set equal to 0.04; q represents the combined corrections for crystal decay and attenuator used; numerical terms arise as a result of the least significant digit of P, B_1, and B_2 not being recorded by the apparatus. Any negative I was reset to zero. All data were retained, *none being rejected as "not significantly above background."*

Unscaled structure factor amplitudes, F^*, and their standard deviations were calculated as

$$F^* = (I/\mathrm{Lp})^{1/2}$$

$$\sigma(F^*) = [\sigma(I)/\mathrm{Lp}]^{1/2} \text{ for } \sigma(I) \geqslant I$$

and

$$\sigma(F^*) = [F^* - \{(F^*)^2 - \sigma(I)/\mathrm{Lp}\}^{1/2}] \text{ for } \sigma(I) < I$$

Absorption corrections were calculated from the measured crystal dimensions and an absorption coefficient of $\mu = 21.36\ \mathrm{cm}^{-1}$ using the program DRAB (by B. G. DeBoer). Maximum and minimum transmission factors were 0.664 and 0.482.

Finally, equivalent pairs of $hk0$ and $\bar{h}k0$ reflections were averaged, and their intensity replaced by their σ^{-2}-weighted average, with appropriately modified standard deviations.

Solution and Refinement of the Structure

Programs used in solving the structure include SFIX (an appreciably modified version of C. T. Prewitt's SFLS5, for structure-factor calculations and full-matrix least-squares refinement), FORDAP (Fourier synthesis, by A. Zalkin), STAN1 (distances, angles, and their estimated standard deviations, by B. G. DeBoer), and ORTEP (thermal ellipsoid drawings, by C. K. Johnson).

Scattering factors for neutral iron, sulfur, oxygen, and carbon were taken from the compilation of Cromer and Waber[11] and were modified both for the real and imaginary components of anomalous dispersion.[12] Scattering factors for hydrogen are those of Mason and Robertson.[13] The function minimized during least-squares refinement processes was $\Sigma w(|F_o| - |F_c|)^2$, where $w(hkl) = \sigma^{-2}[F_o(hkl)]$ and $\sigma[F_o(hkl)]$ is derived from $\sigma[F^*(hkl)]$ by appropriate propagation of absorption corrections and scale factors.

Table I. Final Atomic Coordinates[a] and Isotropic Thermal Parameters[b] for $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$

Atom	x	y	z	B, Å^2
Fe(1)	−0.010095 (36)	0.004417 (15)	0.227700 (22)	2.26
Fe(2)	0.293871 (37)	0.190897 (14)	0.378289 (22)	2.28
S	0.256900 (58)	0.080609 (24)	0.270826 (36)	1.97
O(1)	0.24459 (22)	0.10527 (8)	0.15726 (12)	3.35
O(2)	0.43020 (18)	0.03189 (8)	0.34059 (12)	3.03
O(11)	0.14508 (25)	−0.05458 (12)	0.46595 (14)	4.85
O(12)	0.18579 (29)	−0.11546 (10)	0.16164 (18)	5.18
O(13)	0.62309 (29)	0.22782 (13)	0.33389 (20)	6.06
O(14)	−0.00172 (31)	0.27206 (12)	0.17545 (17)	5.82
C(1)	−0.19993 (33)	0.07892 (16)	0.09390 (21)	4.20
C(2)	−0.24438 (36)	0.00197 (17)	0.05727 (22)	4.45
C(3)	−0.30118 (32)	−0.03640 (19)	0.13385 (27)	4.94
C(4)	−0.29015 (34)	0.01818 (21)	0.21744 (25)	5.04
C(5)	−0.22591 (33)	0.08923 (17)	0.19307 (23)	4.56
C(6)	0.16797 (38)	0.15826 (16)	0.48478 (20)	4.10
C(7)	0.18620 (48)	0.23954 (17)	0.48797 (22)	4.85
C(8)	0.38079 (53)	0.25828 (15)	0.53286 (22)	5.16
C(9)	0.48641 (41)	0.18806 (18)	0.55853 (22)	4.84
C(10)	0.35519 (39)	0.12631 (13)	0.53026 (18)	3.87
C(11)	0.08715 (27)	−0.02929 (12)	0.37385 (18)	2.93
C(12)	0.11228 (29)	−0.06763 (12)	0.18850 (17)	3.05
C(13)	0.49109 (35)	0.21330 (13)	0.34814 (21)	3.75
C(14)	0.11469 (33)	0.23943 (12)	0.25403 (19)	3.37
H(1)	−0.1489 (47)	0.1172 (19)	0.0600 (30)	6.9 (7)
H(2)	−0.2347 (47)	−0.0201 (19)	−0.0026 (31)	7.0 (7)
H(3)	−0.3297 (54)	−0.0838 (23)	0.1439 (36)	8.2 (9)
H(4)	−0.3074 (50)	0.0111 (19)	0.2763 (31)	7.3 (8)
H(5)	−0.2009 (40)	0.1379 (17)	0.2299 (25)	5.9 (6)
H(6)	0.0546 (45)	0.1322 (18)	0.4558 (26)	6.4 (6)
H(7)	0.0840 (50)	0.2766 (21)	0.4666 (30)	7.4 (8)
H(8)	0.4416 (58)	0.3088 (24)	0.5396 (35)	9.0 (10)
H(9)	0.6241 (59)	0.1795 (21)	0.5940 (33)	7.7 (8)
H(10)	0.3791 (39)	0.0718 (18)	0.5363 (25)	6.1 (6)

[a] Estimated standard deviations, shown in parentheses, are right-adjusted to the least significant digit in the preceding number.
[b] "Equivalent isotropic temperature factors" are listed for nonhydrogen atoms. Each corresponds to the average of the mean square displacements along the three principal axes of the anisotropic atomic vibration ellipsoid.

Discrepancy indices used below are

$$R_F = \Sigma||F_o| - |F_c||/\Sigma|F_o|$$

and

$$R_{wF} = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$$

The positions of the two iron atoms and the sulfur atom were readily obtained from a three-dimensional Patterson synthesis. A three-dimensional Fourier map phased by these three atoms led immediately to the location of all remaining nonhydrogen atoms. Refinement of individual atomic positional and isotropic thermal parameters converged with $R_F = 9.1\%$ and $R_{wF} = 12.2\%$. The application of anisotropic thermal parameters to iron and sulfur atoms only, coupled with further refinement of other atomic positional and isotropic thermal parameters, led to $R_F = 7.9\%$ and $R_{wF} = 10.6\%$. Additional refinement, now using anisotropic thermal parameters for all nonhydrogen atoms, led to the reduced discrepancy indices, $R_F = 4.0\%$ and $R_{wF} = 5.2\%$. A difference Fourier synthesis resulted in the unequivocal location of all ten hydrogen atoms. Two cycles of refinement of all atomic positional parameters, anisotropic thermal parameters for nonhydrogen atoms, and isotropic thermal parameters for hydrogen atoms led to convergence at $R_F = 3.4\%$ and $R_{wF} = 4.0\%$.

A survey of low-angle reflections indicated that their $|F_o|$ values were systematically too large. A total of 66 reflections with $(\sin\theta/\lambda) < 0.175$ were corrected for this anomaly, which is an artifact due to absorption by the niobium β filter of the short wavelengths (*i.e.*, $\lambda < 0.65291$ Å[14]) which constitute at least a portion of the initial background of low-angle reflections.[15] A final three cycles led to convergence (*i.e.*, the maximum shift in a parameter was less than 0.1σ) at $R_F = 3.01\%$ and $R_{wF} = 3.63\%$.

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(11) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, 18, 104 (1965).

(12) D. T. Cromer and D. Lieberman, *J. Chem. Phys.*, 53, 1891 (1970).

(13) R. Mason and G. B. Robertson, *Advan. Struct. Res. Diffr. Methods*, 2, 57 (1966).

(14) "International Tables for X-Ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, p 61.

(15) The method of correction is described in detail in ref 10.

Table II. Anisotropic Thermal Parameters for $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}	$\langle U\rangle$[b]
Fe(1)	2.05 (1)	2.64 (1)	2.19 (1)	−0.05 (1)	1.06 (1)	−0.23 (1)	(0.19,0.16,0.16)
Fe(2)	2.79 (1)	1.93 (1)	2.32 (1)	0.07 (1)	1.37 (1)	−0.02 (1)	(0.19,0.16,0.16)
S	2.19 (2)	1.94 (2)	2.17 (2)	0.09 (1)	1.33 (1)	−0.00 (1)	(0.17,0.16,0.14)
O(1)	4.96 (6)	3.18 (6)	2.95 (5)	−0.36 (5)	2.72 (5)	−0.05 (5)	(0.25,0.20,0.15)
O(2)	2.29 (4)	2.89 (6)	3.96 (6)	0.62 (4)	1.49 (4)	0.12 (5)	(0.23,0.20,0.15)
O(11)	4.54 (7)	6.18 (9)	3.47 (7)	−0.95 (7)	1.55 (6)	1.38 (7)	(0.31,0.23,0.18)
O(12)	6.37 (9)	3.77 (7)	5.79 (9)	1.28 (7)	3.14 (8)	−0.94 (7)	(0.30,0.28,0.17)
O(13)	5.60 (10)	6.21 (11)	8.31 (13)	−2.29 (8)	4.87 (10)	−1.18 (9)	(0.35,0.28,0.18)
O(14)	6.98 (11)	5.37 (10)	4.51 (8)	2.95 (8)	2.15 (8)	1.94 (8)	(0.34,0.27,0.18)
C(1)	2.94 (8)	5.31 (12)	3.52 (9)	1.11 (8)	0.76 (7)	1.03 (9)	(0.27,0.24,0.17)
C(2)	3.06 (9)	6.57 (15)	2.73 (9)	0.56 (9)	0.49 (7)	−1.23 (9)	(0.31,0.21,0.17)
C(3)	2.33 (8)	5.53 (15)	5.70 (14)	−1.16 (9)	0.78 (9)	−0.42 (12)	(0.30,0.27,0.16)
C(4)	2.37 (8)	9.07 (19)	4.06 (12)	0.74 (10)	1.81 (8)	0.56 (12)	(0.34,0.23,0.16)
C(5)	2.74 (8)	5.58 (14)	4.22 (11)	1.58 (9)	0.64 (8)	−1.04 (10)	(0.32,0.22,0.16)
C(6)	4.74 (11)	5.46 (12)	3.09 (9)	−0.98 (10)	2.66 (9)	−0.31 (9)	(0.28,0.23,0.16)
C(7)	6.95 (15)	5.05 (13)	3.65 (10)	2.55 (12)	3.40 (11)	0.49 (9)	(0.33,0.22,0.16)
C(8)	8.85 (20)	3.20 (10)	3.43 (10)	−1.23 (11)	2.83 (12)	−1.14 (8)	(0.34,0.22,0.16)
C(9)	3.98 (11)	6.81 (15)	2.71 (9)	−0.10 (10)	0.67 (8)	−0.06 (9)	(0.29,0.26,0.18)
C(10)	6.37 (13)	2.95 (9)	2.44 (8)	0.82 (8)	2.15 (8)	0.52 (7)	(0.29,0.19,0.16)
C(11)	2.58 (6)	3.29 (8)	3.16 (9)	−0.67 (6)	1.53 (6)	0.06 (6)	(0.22,0.20,0.15)
C(12)	3.45 (8)	2.69 (7)	3.09 (8)	−0.15 (6)	1.57 (7)	−0.29 (6)	(0.21,0.20,0.18)
C(13)	4.50 (10)	3.13 (9)	4.17 (10)	−0.97 (8)	2.47 (9)	−0.62 (8)	(0.26,0.21,0.18)
C(14)	4.46 (9)	2.78 (8)	3.23 (8)	0.76 (7)	2.07 (8)	0.28 (7)	(0.25,0.19,0.18)

[a] In units of Å^2 and for the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$. Standard deviations are derived from the inverse of the final least-squares matrix. [b] These are the root-mean-square amplitudes of vibration (in Å) along the three principal axes of the atomic vibration ellipsoid. For orientations, see Figure 1.

The standard deviation in an observation of unit weight or "goodness-of-fit," defined by $[\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{1/2}$, was 1.11; the number of reflections (m) was 3472 and the number of parameters refined (n) was 248, yielding $m/n = 14.0$. The goodness-of-fit was not markedly dependent on θ or on $|F_o|$, thus indicating a correctly chosen weighting scheme.

The correctness of the determined structure was confirmed by a final difference Fourier synthesis on which the maxima were peaks of 0.30 e Å^{-3} [close to the π-cyclopentadienyl ring attached to Fe(2)] and 0.29 e Å^{-3} [close to the position of Fe(1)] and the minima were "holes" of −0.30 e Å^{-3} [close to the position of Fe(2)] and −0.30 e Å^{-3} (close to the sulfur atom). Data were inspected for evidence of extinction; none was found.

A table of observed and calculated structure factor amplitudes is available.[16] Positional and isotropic thermal parameters are collected in Table I; anisotropic thermal parameters for nonhydrogen atoms are listed in Table II.

Molecular Structure

Interatomic distances, with their estimated standard deviations (esd's), are collected in Table III; bond angles (with esd's) are shown in Table IV. The labeling of atoms and the overall molecular stereochemistry is depicted in Figure 1, which also shows the 50% probability contours of the atomic vibration ellipsoids for nonhydrogen atoms.

The crystal contains isolated molecules of $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$, mutually separated by normal van der Waals distances. As expected, the molecule consists of two $\pi\text{-}C_5H_5Fe(CO)_2$ units which are bridged by an SO_2 moiety; bridging occurs *via* two iron–sulfur linkages.

Each iron atom may be regarded formally as a d^7 Fe(I) ion which achieves the appropriate noble gas configuration by the donation of six electrons from a π-cyclopentadienyl anion, two electrons from each of two carbonyl ligands, and one electron from the SO_2 fragment. The iron atoms have a pseudo-octahedral coordination sphere since they are linked by three covalent bonds to carbonyl and SO_2 ligands and by a complex π-electron system to a formally tridentate $\pi\text{-}C_5H_5$ ligand. The geometry about the iron may more graphically be described as "resembling a three-legged piano-stool."

Table III. Interatomic Distances (in Å) for $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$[a]

Atoms	Distance	Atoms	Distance
	(a) Distances from Iron Atoms		
Fe(1)· · ·Fe(2)	3.9090 (8)		
Fe(1)–S	2.2790 (6)	Fe(2)–S	2.2814 (7)
Fe(1)–C(1)	2.099 (3)	Fe(2)–C(6)	2.086 (2)
Fe(1)–C(2)	2.099 (3)	Fe(2)–C(7)	2.109 (2)
Fe(1)–C(3)	2.116 (2)	Fe(2)–C(8)	2.122 (2)
Fe(1)–C(4)	2.113 (2)	Fe(2)–C(9)	2.097 (3)
Fe(1)–C(5)	2.097 (2)	Fe(2)–C(10)	2.101 (2)
Fe(1)–C(11)	1.768 (2)	Fe(2)–C(13)	1.775 (2)
Fe(1)–C(12)	1.763 (2)	Fe(2)–C(14)	1.765 (2)
Fe(1)· · ·O(11)	2.907 (2)	Fe(2)· · ·O(13)	2.914 (2)
Fe(1)· · ·O(12)	2.900 (2)	Fe(2)· · ·O(14)	2.905 (2)
	(b) Distances within SO_2 Fragment		
S–O(1)	1.4797 (15)	S–O(2)	1.4764 (14)
	(c) Carbon–Carbon Distances within π-Cyclopentadienyl Ligands		
C(1)–C(2)	1.390 (4)	C(6)–C(7)	1.400 (4)
C(2)–C(3)	1.411 (4)	C(7)–C(8)	1.373 (5)
C(3)–C(4)	1.398 (5)	C(8)–C(9)	1.405 (4)
C(4)–C(5)	1.404 (4)	C(9)–C(10)	1.392 (4)
C(5)–C(1)	1.389 (4)	C(10)–C(6)	1.394 (4)
	(d) Carbon–Hydrogen Distances		
C(1)–H(1)	0.97 (3)	C(6)–H(6)	0.90 (3)
C(2)–H(2)	0.89 (3)	C(7)–H(7)	0.95 (3)
C(3)–H(3)	0.87 (4)	C(8)–H(8)	0.97 (4)
C(4)–H(4)	0.83 (4)	C(9)–H(9)	0.95 (4)
C(5)–H(5)	0.93 (3)	C(10)–H(10)	0.95 (3)
	(e) Distances within Carbonyl Ligands		
C(11)–O(11)	1.140 (3)	C(13)–O(13)	1.141 (3)
C(12)–O(12)	1.137 (3)	C(14)–O(14)	1.141 (3)

[a] Distances are not corrected for thermal motion. Esd's include errors in the unit cell dimensions and the effect of all positional correlation factors of magnitude >0.1.

The simple ligands are disposed fairly regularly about the iron atoms. Angles around Fe(1) are S-Fe(1)-C(11) = 92.11 (6)°, S-Fe(1)-C(12) = 85.99 (7)°, and C(11)-Fe-C(12) = 93.08 (9)°; analogous angles around Fe(2) are S-Fe(2)-C(13) = 85.87 (8)°, S-Fe(2)-C(14) = 90.95 (7)°, and C(13)-Fe(2)-C(14) = 95.24 (11)°.

[16] A listing of observed and calculated structure-factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth Street, N.W., Washington Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-1646.

Table IV. Angles (in degrees)[a]

(a) Angles around Iron Atoms			
C(1)-Fe(1)-C(2)	38.68 (11)	C(6)-Fe(2)-C(7)	38.99 (11)
C(2)-Fe(1)-C(3)	39.10 (11)	C(7)-Fe(2)-C(8)	37.87 (14)
C(3)-Fe(1)-C(4)	38.60 (13)	C(8)-Fe(2)-C(9)	38.91 (12)
C(4)-Fe(1)-C(5)	38.97 (12)	C(9)-Fe(2)-C(10)	38.73 (11)
C(5)-Fe(1)-C(1)	38.67 (10)	C(10)-Fe(2)-C(6)	38.91 (10)
S-Fe(1)-C(11)	92.11 (06)	S-Fe(2)-C(13)	85.87 (08)
S-Fe(1)-C(12)	85.99 (07)	S-Fe(2)-C(14)	90.95 (07)
C(11)-Fe(1)-C(12)	93.08 (09)	C(13)-Fe(2)-C(14)	95.24 (11)
(b) Angles around Sulfur Atom			
Fe(1)-S-Fe(2)	118.00 (02)	O(1)-S-O(2)	112.91 (08)
Fe(1)-S-O(1)	106.51 (06)	Fe(2)-S-O(1)	107.04 (06)
Fe(1)-S-O(2)	106.54 (06)	Fe(2)-S-O(2)	106.06 (06)
(c) Angles in Carbonyl Groups			
Fe(1)-C(11)-O(11)	176.48 (20)	Fe(2)-C(13)-O(13)	177.02 (24)
Fe(1)-C(12)-O(12)	177.79 (20)	Fe(2)-C(14)-O(14)	178.34 (20)
(d) C-C-C Angles in π-Cyclopentadienyl Ligands			
C(5)-C(1)-C(2)	108.31 (24)	C(10)-C(6)-C(7)	107.99 (24)
C(1)-C(2)-C(3)	108.31 (23)	C(6)-C(7)-C(8)	108.72 (24)
C(2)-C(3)-C(4)	107.16 (27)	C(7)-C(8)-C(9)	107.42 (24)
C(3)-C(4)-C(5)	108.23 (25)	C(8)-C(9)-C(10)	108.62 (26)
C(4)-C(5)-C(1)	107.99 (24)	C(9)-C(10)-C(6)	107.24 (23)
(e) C-C-H Angles in π-Cyclopentadienyl Ligands			
C(5)-C(1)-H(1)	126 (2)	C(10)-C(6)-H(6)	127 (2)
C(2)-C(1)-H(1)	125 (2)	C(7)-C(6)-H(6)	125 (2)
C(1)-C(2)-H(2)	126 (2)	C(6)-C(7)-H(7)	127 (2)
C(3)-C(2)-H(2)	125 (2)	C(8)-C(7)-H(7)	124 (2)
C(2)-C(3)-H(3)	136 (3)	C(7)-C(8)-H(8)	129 (2)
C(4)-C(3)-H(3)	116 (3)	C(9)-C(8)-H(8)	123 (2)
C(3)-C(4)-H(4)	128 (2)	C(8)-C(9)-H(9)	130 (2)
C(5)-C(4)-H(4)	123 (2)	C(10)-C(9)-H(9)	121 (2)
C(4)-C(5)-H(5)	132 (2)	C(9)-C(10)-H(10)	130 (2)
C(1)-C(5)-H(5)	120 (2)	C(6)-C(10)-H(10)	123 (2)

[a] See footnote *a* to Table III.

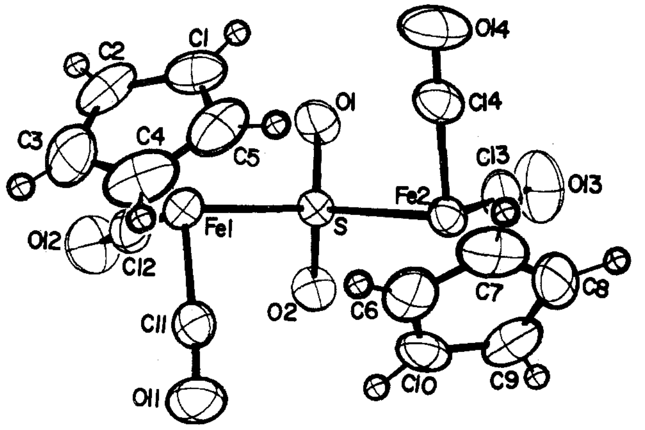


Figure 1. Labeling of atoms in the $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$ molecule. This ORTEP diagram shows the 50% probability envelopes for the vibration ellipsoids of nonhydrogen atoms. Hydrogen atoms are shown (artificially reduced) as spheres of 0.1-Å radius.

Each of the π-cyclopentadienyl rings has D_{5h} symmetry within the limits of experimental error. Within the system C(1)-C(2)-C(3)-C(4)-C(5), carbon-carbon bond lengths range from 1.389 (4) to 1.411 (4) Å, averaging 1.398 Å, and internal C-C-C angles range from 107.16 (27) to 108.31 (23)°, averaging 108.00°. Corresponding values for the system C(6)-C(7)-C(8)-C(9)-C(10) are C-C = 1.373 (5)-1.405 (4) Å, averaging 1.393 Å, and ∠(C-C-C) = 107.24 (23)-108.72 (24)°, averaging 108.00°. The accepted value for a C-C (π-cyclopentadienyl) bond is ~1.43 Å; the systematically short distances that we observe presumably result from libration of these five-membered carbocyclic rings.[17]

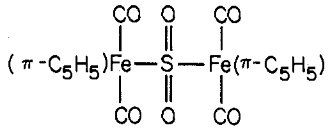
Within the two π-cyclopentadienyl systems, carbon-hydrogen distances range from 0.83 (4) to 0.97 (4) Å, with a mean value of 0.92 Å; this distance is, of course, systematically reduced from the accepted C-H distance of ~1.08 Å. This is a result characteristic of X-ray diffraction (as opposed to neutron diffraction, electron diffraction, or spectroscopic) studies and results from the use of a spherically symmetric scattering factor for hydrogen when, in fact, the electron density around hydrogen is "pear-shaped," being elongated in the direction of the hydrogen-carbon σ bond.

The 20 C-C-H angles range from 116 (3) to 136 (3)°, averaging 126°, the angle expected as the external bisector of a regular pentagonal angle of 108°.

The ten Fe-C (π-cyclopentadienyl) distances range from 2.086 (2) to 2.122 (2) Å, averaging 2.104 Å, as compared to values of 2.089 Å in $[\pi\text{-}C_5H_5Fe(CO)_2]_2C_4H_4$[18] and 2.094 Å in $\pi\text{-}C_5H_5Fe(CO)_2C_4H_5SO_2$.[4]

Bond distances involving the four carbonyl ligands are quite normal and are internally consistent, with Fe-CO = 1.763 (2)-1.775 (2) Å (av 1.768 Å) and C-O = 1.137 (3)-1.141 (2) Å (av 1.140 Å); for comparison, we may note that the corresponding distances in the $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CHC_6H_5$ molecule[5] are Fe-CO = 1.766 Å (av), C-O = 1.145 Å (av). Within the present molecule, Fe-C-O angles are close to 180°, individual values ranging from Fe(1)-C(11)-O(11) = 176.48 (20)° to Fe(2)-C(14)-O(14) = 178.34 (20)°. As has been pointed out by Kettle,[19] M-C-O systems are not expected to be precisely linear except in situations of high molecular symmetry; such exceptions do not pertain to the present case.

The iron-sulfur distances are Fe(1)-S = 2.2790 (6) Å and Fe(2)-S = 2.2814 (7) Å, the mean value being 2.2802 Å. The Fe(1)· · ·Fe(2) distance of 3.9090 (8) Å is clearly outside of normal bonding range. The molecule can therefore be represented schematically by structure I. It is interesting



$$\begin{array}{ccccc} & CO & O & CO & \\ & | & \| & | & \\ (\pi\text{-}C_5H_5) & Fe & {-}S{-} & Fe & (\pi\text{-}C_5H_5) \\ & | & \| & | & \\ & CO & O & CO & \end{array}$$

I

to note that the mean iron-sulfur distance of 2.2802 Å in this molecule is considerably longer than that found in the $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CHC_6H_5$ molecule[5] (Fe-S = 2.218 (2) Å) but is still shorter than the value expected for an iron-sulfur bond of unit bond order [~2.38 Å, using Pauling's value of 1.04 Å for the covalent radius of tetrahedrally coordinated sulfur[20] and Churchill's value of 1.34 Å for the covalent radius of iron in $\pi\text{-}C_5H_5Fe(CO)_2X$ species[21]]. Clearly, there is appreciable multiple bond character in these iron-sulfur linkages.

The central sulfur atom has a slightly distorted tetrahedral stereochemical environment, with Fe(1)-S-Fe(2) = 118.00 (2)°, O(1)-S-O(2) = 112.91 (8)°, Fe(1)-S-O(1) = 106.51 (6)°, Fe(1)-S-O(2) = 106.54 (6)°, Fe(2)-S-O(1) = 107.04 (6)°, and Fe(2)-S-O(2) = 106.06 (6)°. The sulfur-oxygen bond lengths, S-O(1) = 1.4797 (15) Å and S-O(2) = 1.4764 (14) Å, are closely similar to the S=O bond length of 1.480 (8) Å observed in $\pi\text{-}C_5H_5Fe(CO)_2C_4H_5SO_2$ (which has structure II).[4]

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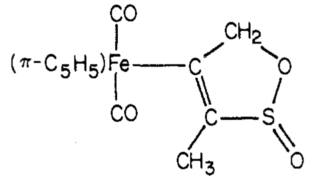
(17) *Cf.* P. J. Wheatley, *Perspect. Struct. Chem.*, 1, 9 (1967).

(18) M. R. Churchill and J. Wormald, *Inorg. Chem.*, 8, 1936 (1969).

(19) S. F. A. Kettle, *Inorg. Chem.*, 4, 1611 (1965).

(20) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 246.

(21) M. R. Churchill, *Perspect. Struct. Chem.*, 3, 91 (1970); see, especially, Appendix I, p 157.



II

Finally, we may note that the present complex readily decomposes in solution forming $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$; an X-ray crystallographic characterization of this new species is currently in progress.[22]

Registry No. $[\pi\text{-}C_5H_5Fe(CO)_2]_2SO_2$, 38999-15-4.

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[22] M. R. Churchill and K. L. Kalra, *Inorg. Chem.*, 12, 1650 (1973).

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Crystallographic Studies on Sulfur Dioxide Insertion Compounds. V.[1] Elucidation of the Molecular Geometry of *cis*-μ-Carbonyl-μ-(sulfur dioxide)-bis(π-cyclopentadienylcarbonyliron), *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$

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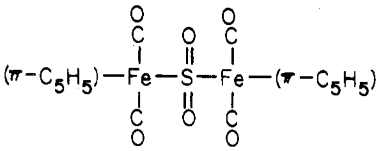
cis-μ-Carbonyl-μ-(sulfur dioxide)-bis(π-cyclopentadienylcarbonyliron), *cis*-$(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$, crystallizes in the centrosymmetric orthorhombic space group *Pbca* [D_{2h}^{15}; No. 61] with $a = 22.461$ (3), $b = 11.470$ (2), and $c = 21.415$ (3) Å. The measured and calculated densities are respectively 1.865 (10) and 1.878 g cm^{-3} for $Z = 16$. The asymmetric unit contains two $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ molecules. Single-crystal X-ray diffraction data complete to $2\theta = 46.5°$ (Mo Kα radiation) were collected with a Picker FACS-1 diffractometer, and the structure was solved by means of conventional Patterson and Fourier techniques. Least-squares refinement of atomic positional and thermal parameters, with hydrogen atoms included in calculated positions, converged with $R_F = 5.18\%$ and $R_{wF} = 3.68\%$ for 3975 independent reflections. The two independent molecules have essentially identical conformations, each consisting of two $(\pi\text{-}C_5H_5)Fe(CO)$ units linked by a direct iron–iron bond which is bridged symmetrically by a carbonyl and a sulfur dioxide ligand. The molecule has an overall cis geometry.

Introduction

We have recently become interested in molecular species in which sulfur dioxide acts as a bridge between two (or more) metal atoms and we have reported the crystal structure of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$[1,2] in which the two iron atoms are bridged *only* by a sulfur dioxide ligand (as shown in I).

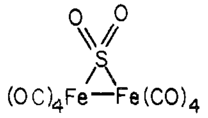


$$(\pi\text{-}C_5H_5)\text{—}Fe(CO)_2\text{—}SO_2\text{—}Fe(CO)_2\text{—}(\pi\text{-}C_5H_5)$$

I

A by-product in the synthesis of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$ is $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$;[2] this new molecule also results from the decomposition of $[(\pi\text{-}C_5H_5)Fe(CO)_2]_2(SO_2)$. The present article concerns the crystallographic characterization of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$.

It may be noted that the results of X-ray diffraction studies have been reported for at least one other species in which sulfur dioxide bridges two metal atoms; the molecular structure of $Fe_2(CO)_8(SO_2)$ (II) has been examined, independently, by two research groups.[3,4]



II

Collection and Reduction of X-Ray Diffraction Data

A sample of $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3(SO_2)$ was provided by Professor A. Wojcicki of The Ohio State University. Preliminary optical examination showed beautifully formed red octahedra (presumably with well-developed {111} faces). However, these faces had a "matte" appearance, rather than being lustrous. Upon poking with a needle the "crystals" crumbled to powder, indicating that the original material has decomposed at some stage. Careful microexcavation of the rubble formed from some of the larger "crystals" did, however, lead to our obtaining some more-or-less ellipsoidal single crystals, the surfaces of which closely resembled that of a well-dried prune. Discussions with Professor Wojcicki indicated that the method of production of this material had not yet been optimized, that its stability in solution was uncertain, and that recrystallization was not recommended.

A single-crystal X-ray diffraction study was therefore undertaken on a highly nonideal "prune-shaped" crystal of length ~0.3 mm and maximum radius ~0.1 mm.

Preliminary examination of the crystal was carried out using precession and cone-axis photographs, thereby demonstrating the D_{2h} Laue symmetry of the diffraction pattern, obtaining approximate cell dimensions, and revealing the systematic absences $0kl$ for $k = 2n + 1$, $h0l$ for $l = 2n + 1$, and $hk0$ for $h = 2n + 1$, consistent only with the centrosymmetric orthorhombic space group *Pbca* (D_{2h}^{15}; No. 61).

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[1] Part IV: M. R. Churchill, B. G. DeBoer, and K. L. Kalra, *Inorg. Chem.*, 12, 1646 (1973).

[2] M. R. Churchill, B. G. DeBoer, K. L. Kalra, P. Reich-Rohrwig, and A. Wojcicki, *J. Chem. Soc., Chem. Commun.*, 981 (1972).

[3] J. Meunier-Piret, P. Piret, and M. van Meerssche, *Bull. Soc. Chim. Belg.*, 76, 374 (1967).

[4] R. F. Bryan and P. T. Greene, to be submitted for publication.