Crystal Structure of Dicarbonyl(π-cyclopentadienyl)(pentafluorophenylsulphonyl-*S*)iron

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The product of the reaction between $C_6F_5SO_2Cl$ and the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$ is the air-stable compound $C_6F_5SO_2Fe(CO)_2(\pi\text{-}C_5H_5)$. This orange complex crystallizes in the monoclinic system, space group $P2_1/c$, $a = 10{\cdot}97(2)$, $b = 12{\cdot}12(2)$, $c = 12{\cdot}06(2)$ Å, $\beta = 117{\cdot}6(2)°$, $Z = 4$. The crystal structure analysis based on 754 non-zero independent reflections has resulted in a final R 10·7% and shows the compound to be an *S*-sulphinato-complex.

A LARGE number of transition metal sulphinate complexes have been prepared by sulphur dioxide insertion into a metal–carbon σ bond with the subsequent formation of a metal–sulphur linkage.[1] However this method was not successful in the preparation of $C_6F_5SO_2Fe(CO)_2(\pi\text{-}C_5H_5)$ (I) which was prepared by nucleophilic attack on $C_6F_5SO_2Cl$ using the anion $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$.[2] This investigation was carried out in order to confirm the presence of the *S*-sulphinato-group and to provide structural information to support the interpretation of the ^{19}F n.m.r. spectrum of the compound reported previously.[3]

EXPERIMENTAL

Crystal Data.—$C_{13}H_5F_5FeO_4S$, $M = 408$, Monoclinic, $a = 10{\cdot}97(2)$, $b = 12{\cdot}12(2)$, $c = 12{\cdot}06(2)$ Å, $\beta = 117{\cdot}6(2)°$, $U = 1420$ Å^3, $D_m = 1{\cdot}90$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}91$ g cm^{-3}, $F(000) = 808$, $\mu(\text{Mo-}K_\alpha) = 13{\cdot}2$ cm^{-1}, data layers 0—2*kl*, *hk*0—2, Space group, $P2_1/c$ (C_{2h}^5, No. 14), crystal dimensions *ca.* $0{\cdot}5 \times 0{\cdot}1 \times 0{\cdot}07$ mm. A total of 893 independent reflections was recorded by visual estimation from precession photographs taken with Mo-K_α radiation ($\lambda = 0{\cdot}7107$ Å). Of these 139 were found to be too weak to be estimated by the visual technique employed. No correction was made for absorption.

The structure was solved by standard heavy-atom procedures and refined by using full-matrix least-squares methods. All atoms were refined with isotropic thermal parameters, and in the final calculations hydrogen atoms in positions calculated using the cyclopentadienyl group were incorporated into the model. The positional and thermal parameters of the hydrogen atoms were not refined. The final weighting scheme was $w = (7 + 0{\cdot}3F_o + 0{\cdot}001F_o^2)^{-1}$ which gave a satisfactory analysis of $w\Delta^2$ in ranges of F_o and $(\sin\theta/\lambda)^2$. The final value of R over 754 non-zero reflections was 10·7% and a final difference map revealed no fluctuations greater than ± 1 eÅ^{-3}.

All calculations were carried out on the Salford University KDF 9 computer using local versions of programs written for the KDF 9 by J. S. Rollett and G. Ford.

RESULTS

The final atomic co-ordinates and thermal parameters with their standard deviations are given in Table 1. Details of the molecular geometry are given in Table 2 with standard deviations in parentheses. Figure 1 indicates the labelling of the atoms. The measured and calculated

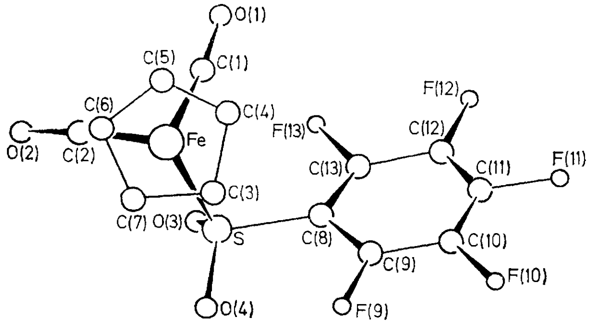

FIGURE 1 View of the molecule showing the numbering system

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[1] J. P. Bibler and A. J. Wojcicki, *J. Amer. Chem. Soc.*, 1966, **88**, 4862.

[2] M. I. Bruce and A. D. Redhouse, *J. Organometallic Chem.*, 1971, **30**, C78.

[3] M. I. Bruce, *J. Chem. Soc.* (*A*), 1968, 1459.

structure factors are listed in Supplementary Publication No. SUP 20976 (5 pp.).*

TABLE 1

Atomic parameters

Atom	x/a	y/b	z/c	$U/Å^2$
Fe	0·1242(3)	0·2066(3)	−0·1658(2)	0·0415(9)
S	0·2880(3)	0·3071(6)	−0·1721(4)	0·0489(14)
C(1)	0·0855(19)	0·3068(20)	−0·0837(16)	0·0488(48)
O(1)	0·0498(15)	0·3693(15)	−0·0303(13)	0·0764(44)
C(2)	0·0055(22)	0·2539(20)	−0·3130(19)	0·0527(56)
O(2)	−0·0741(16)	0·2936(14)	−0·4080(14)	0·0762(43)
O(3)	0·2407(15)	0·4160(15)	−0·2208(12)	0·0685(44)
O(4)	0·3623(14)	0·2498(13)	−0·2296(12)	0·0601(41)
C(3)	0·2577(27)	0·0692(28)	−0·0962(24)	0·0912(86)
C(4)	0·1885(25)	0·0858(29)	−0·0244(21)	0·0791(75)
C(5)	0·0566(28)	0·0776(30)	−0·1006(23)	0·0807(78)
C(6)	0·0256(26)	0·0528(28)	−0·2175(22)	0·0886(78)
C(7)	0·1521(22)	0·0528(23)	−0·2202(19)	0·0696(61)
C(8)	0·4165(18)	0·3331(19)	−0·0098(15)	0·0438(42)
C(9)	0·5332(22)	0·2662(23)	0·0516(19)	0·0549(58)
C(10)	0·6279(24)	0·2863(26)	0·1736(21)	0·0708(63)
C(11)	0·6086(23)	0·3652(23)	0·2377(20)	0·0577(57)
C(12)	0·5016(23)	0·4351(23)	0·1851(19)	0·0579(59)
C(13)	0·4086(22)	0·4178(23)	0·0611(18)	0·0587(58)
F(9)	0·5567(15)	0·1761(15)	−0·0063(14)	0·0920(47)
F(10)	0·7377(16)	0·2151(17)	0·2302(14)	0·0994(47)
F(11)	0·7048(13)	0·3847(13)	0·3604(11)	0·0806(38)
F(12)	0·4808(15)	0·5162(15)	0·2491(13)	0·0928(48)
F(13)	0·2977(14)	0·4845(15)	0·0118(12)	0·0895(45)
H(3)	0·3679	0·0667	−0·0647	0·1
H(4)	0·2267	0·1102	0·0751	0·1
H(5)	−0·0207	0·0874	−0·0676	0·1
H(6)	−0·0763	0·0418	−0·2954	0·1
H(7)	0·1662	0·0404	−0·3013	0·1

DISCUSSION

The analysis confirms the descriptions of (I) as an *S*-sulphinato-complex. The Fe–S distance is 2·20(1) Å which, if following Churchill[4] we take the length of an Fe–S single bond to be 2·38 Å, is significantly shorter than the single bond length. This is in accord with the observations made on the structure of $[\pi\text{-}C_5(CH_3)_5]Fe(CO)_2SO_2CH_2CH{=}CHC_6H_5$[4] where the Fe–S bond length is 2·218 Å.

The S–C(8) bond length is 1·83(2) Å and is close to the single bond distance of 1·78 Å calculated from the covalent radii of sulphur (1·04 Å) and sp^2 carbon (0·74 Å). This fact, together with the short Fe–S distance, can be taken to indicate a strong π-interaction between the iron and sulphur *d* orbitals, but minimal interaction between the π system of the phenyl group and the sulphur *d* orbitals, and supports the interpretation of the ^{19}F n.m.r. spectrum of (I).[3]

The co-ordination polyhedron of the iron atom is similar to that found in a number of complexes containing the $(\pi\text{-}C_5H_5)Fe(CO)_2$ group, *i.e.* the iron can be considered to be pseudo-octahedrally co-ordinated. The distances of the iron to the cyclopentadienyl carbon atoms range from 2·04 to 2·12(4) Å, the mean value of which (2·08 Å) compares favourably with the value of 2·04 Å reported by Wheatley[5] as the mean of a number of previous determinations. The other three ligands are disposed around the iron atom in a manner consistent with octahedral co-ordination and the structural parameters associated with the two carbonyl groups are normal. The sulphur has a tetrahedral environment which deviates somewhat from regularity (see Table 2).

TABLE 2

(a) Intramolecular distances/Å with estimated standard deviations in parentheses

Fe–S	2·201(6)	C(5)–C(6)	1·32(4)
Fe–C(1)	1·74(2)	C(6)–C(7)	1·40(4)
Fe–C(2)	1·74(2)	C(7)–C(3)	1·42(4)
Fe–C(3)	2·12(3)	C(8)–C(9)	1·40(4)
Fe–C(4)	2·10(3)	C(9)–C(10)	1·37(3)
Fe–C(5)	2·04(3)	C(10)–C(11)	1·30(4)
Fe–C(6)	2·10(3)	C(11)–C(12)	1·34(4)
Fe–C(7)	2·05(3)	C(12)–C(13)	1·38(3)
S–O(3)	1·44(2)	C(13)–C(8)	1·37(3)
S–O(4)	1·47(2)	C(9)–F(9)	1·38(3)
S–C(8)	1·83(2)	C(10)–F(10)	1·38(3)
C(1)–O(1)	1·17(3)	C(11)–F(11)	1·38(3)
C(2)–O(2)	1·17(3)	C(12)–F(12)	1·33(3)
C(3)–O(3)	1·41(4)	C(13)–F(13)	1·35(3)
C(4)–C(5)	1·31(4)		

(b) Intramolecular angles (°)

Fe–C(1)–O(1)	174(2)	S–C(8)–C(13)	124(2)
Fe–C(2)–O(2)	175(2)	C(9)–C(8)–C(13)	114(2)
Fe–S–O(3)	112(1)	F(9)–C(9)–C(8)	122(2)
Fe–S–O(4)	113(1)	F(9)–C(9)–C(10)	117(2)
Fe–S–C(8)	107(1)	C(8)–C(9)–C(10)	121(2)
O(3)–S–O(4)	115(1)	F(10)–C(10)–C(9)	118(2)
O(3)–S–C(8)	103(1)	F(10)–C(10)–C(11)	121(2)
O(4)–S–C(8)	105(1)	C(9)–C(10)–C(11)	121(2)
C(1)–Fe–C(2)	95(1)	F(11)–C(11)–C(10)	120(2)
C(1)–Fe–S	93(1)	F(11)–C(11)–C(12)	118(2)
C(2)–Fe–S	91(1)	C(10)–C(11)–C(12)	122(2)
C(3)–C(4)–C(5)	107(2)	F(12)–C(12)–C(11)	122(2)
C(4)–C(5)–C(6)	115(2)	F(12)–C(12)–C(13)	120(2)
C(5)–C(6)–C(7)	105(2)	C(11)–C(12)–C(13)	118(2)
C(6)–C(7)–C(8)	108(2)	F(13)–C(13)–C(8)	119(2)
C(7)–C(8)–C(3)	105(2)	F(13)–C(13)–C(12)	117(2)
S–C(8)–C(9)	122(2)	C(8)–C(13)–C(12)	124(2)

(c) Least squares planes defined by atomic positions

In the following equations *X*, *Y*, *Z* refer to orthogonal co-ordinates obtained by the transformation:

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a\sin\beta & 0 & 0 \\ 0 & b & 0 \\ a\cos\beta & 0 & c \end{bmatrix} \begin{bmatrix} x/a \\ y/b \\ z/c \end{bmatrix}$$

(1) Plane defined by C(3), C(4), C(5), C(6), and C(7)

$$0{\cdot}0575X - 0{\cdot}9813Y + 0{\cdot}1838Z + 1{\cdot}1478 = 0$$

Distances of atoms from the planes (Å)

C(3) 0·015, C(4) 0·002, C(5) −0·020, C(6) 0·028, C(7) −0·025

(2) Plane defined by C(8), C(9), C(10), C(11), C(12), and C(13)

$$-0{\cdot}5211X - 0{\cdot}6027Y + 0{\cdot}6043Z + 5{\cdot}9111 = 0$$

Distances of atoms from the plane (Å)

C(8) 0·018, C(9) 0·004, C(10) −0·024, C(11) 0·023, C(12) 0·000, C(13) −0·020, F(9) 0·048, F(10) 0·014, F(11) −0·008, F(12) 0·043, F(13) 0·036

The largest sulphur bond angle is that involving the two oxygen atoms and is considerably larger than the regular tetrahedral angle. This feature has been observed in the structures of a variety of compounds containing the

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index issue. Items less than 10 pp. are sent as full-size copies.

[4] M. R. Churchill and J. Wormald, *Inorg. Chem.*, 1971, **10**, 572.

[5] P. J. Wheatley, 'Perspectives in Structural Chemistry,' eds. J. D. Dunitz and J. A. Ibers, Wiley, New York, 1967, vol. 1, p. 1.

SO_2 group.[6] The S–O distances of 1·44(2) Å and 1·47(2) Å are close to accepted values.[6]

The phenyl and the cyclopentadienyl groups are accurately planar (see Table 2) with mean C–C distances of 1·36 and 1·37 Å respectively. The phenyl group makes an angle of 86° with the plane defined by Fe, S, C(8), C(11), and F(11). This angle is presumably influenced by steric factors as rotation of the phenyl group about the S–C bond would involve the *o*-fluorine atoms in close approaches with atoms O(1), O(4), O(3) and the hydrogen atom associated with C(3). These intramolecular approaches are F(9)—O(4) 2·70, F(9)—H(3) 2·28, F(13)—O(1) 2·89, and F(13)—O(3) 2·71 Å for the observed arrangement (see Figure 2).

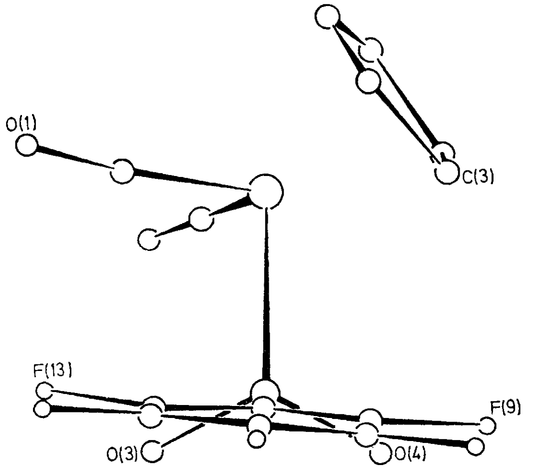

FIGURE 2 View showing the orientation of the pentafluorophenyl group with respect to the rest of the molecule

The average C–F bond length is 1·36 Å compared with the accepted value of 1·328(5) Å for a C(aromatic)—F distance.[7]

The molecules are separated by the usual van der Waals distances (Table 3).

TABLE 3

Closest intermolecular approaches/Å

S–H(4^{I})	2·98	O(4)–H(4^{I})	2·72
O(1)–H(7^{II})	2·68	F(9)–F(11^{I})	2·86
O(2)–F(11^{III})	2·94	F(11)–H(4^{V})	2·85
O(2)–H(5^{I})	2·68	F(11)–H(5^{VI})	2·74
O(3)–H(4^{I})	2·42	F(13)–H(6^{IV})	2·70
O(3)–H(6^{IV})	2·44		

The superscripts refer to the positions:

I	$x, \frac{1}{2} - y, -\frac{1}{2} + z$	IV	$-x, \frac{1}{2} + y, -\frac{1}{2} - z$
II	$x, \frac{1}{2} - y, \frac{1}{2} + z$	V	$1 - x, \frac{1}{2} + y, \frac{1}{2} - z$
III	$-1 + x, y, -1 + z$	VI	$1 + x, \frac{1}{2} - y, \frac{1}{2} + z$

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[6] S. C. Abrahams, *Quart. Rev.*, 1956, 407.

[7] Interatomic Distances Supplement, *Chem. Soc. Special Publ.*, No. 18, 1965.