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PHOTOINDUCED REACTION OF SULFUR WITH CYCLOPENTADIENYLIRON DICARBONYL DIMER AND CRYSTAL STRUCTURE OF BIS(CYCLOPENTADIENYLIRON)MONOCARBONYL TETRASULFIDE

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Summary

The photolysis of $(\pi^5\text{-}C_5H_4RFe(CO)_2)_2$ with R = H or CH_3, in the presence of elemental sulfur, produces a mixture of organometallic tetrasulfides containing four sulfur and two iron atoms. The structure of one of such compounds has been determined by X-ray diffraction. It contains a core of four sulfur atoms between two irons. One iron is symmetrically linked to four sulfur atoms and to the cyclopentadienyl ring; the other iron is linked to only two sulfur atoms, one carbonyl, and a cyclopentadienyl group.

Introduction

The reactions of cyclooctasulfur with transition metal complexes are known to proceed thermally [1,2] and photochemically [3—5], but examples of reactions are rather rare. Recently, Schunn and his colleagues, by reaction of cyclooctasulfur in presence of $(\pi^5\text{-}C_5H_5Fe(CO)_2)_2$ obtained a complex which could be considered as a model of the active centre of the ferredoxins [1]. Because of the importance of such complexes in numerous catalytic electron-transfer processes [6], we have attempted a photochemical approach to them.

Results and discussion

Photolysis of a saturated methanolic solution of cyclooctasulfur containing $(\pi^5\text{-}C_5H_4RFe(CO)_2)_2$ (R = H, CH_3), produces mainly a major green product. The molecular weight in chloroform viz. ca. 400, shows that the complex is a monomer. The mass spectrum shows in addition to the parent ion at M^+ 398, intense peaks at *m/e* 370, 306, 241, and 176 due to successive loss of the carbonyl group, sulfur atoms, and the cyclopentadienyl group. The elementary analysis is in agreement with $(\pi^5\text{-}C_5H_4RFeS_2)_2CO$ (R = H, CH_3).

The infrared spectrum, at low frequencies, shows two bands at 438 and 415 cm^{-1}, undoubtedly due to ν(S—S) [1,7—9], and several other new bands situated at 184, 203, 244, 314, and 370 cm^{-1}, due to the vibrations of the Fe—S bond [10—13]. The infrared spectrum of solutions in the 1000—2100 cm^{-1} region show characteristic bands of the π^5-C_5H_5Fe group [14] and strong bands at 1950 and 1985 cm^{-1} due to ν(CO) vibrations of bonded carbonyl. There are no characteristic bands of bridged carbonyls.

The infrared spectrum is markedly solvent dependent in the 1700—2000 cm^{-1} region; with non-polar solvents such as carbon disulfide, benzene, toluene, cyclohexane, the ν(CO) at 1985 cm^{-1} is weak, while the ν(CO) at 1950 cm^{-1} is strong; in more polar solvents such as carbon tetrachloride, chloroform, dimethyl sulfoxide, dimethyl formamide and pyridine the reverse is true.

The ^{13}C NMR spectrum indicates that there is only one carbonyl group, suggesting that there are several forms of the complex in solution. The ^{1}H NMR confirms this. Recrystallisation of the green complex obtained from the reaction with methylcyclopentadienyliron dicarbonyl dimer gave crystals suitable for X-ray studies, and the complete structure and stereochemistry of this derivative were determined.

A perspective view of the molecule with atom numbering is shown in Fig. 1. The atomic coordinates and thermal parameters are listed in Table 1. Tables 2 and 3 give interatomic distances and valence angles. Important planes are given in Table 4. The salient structural feature of this molecule is that the two Fe atoms are in quite different environments. The non-bonding distance between the two Fe atoms is 3.397(4) Å. The six Fe—S distances have a mean value of

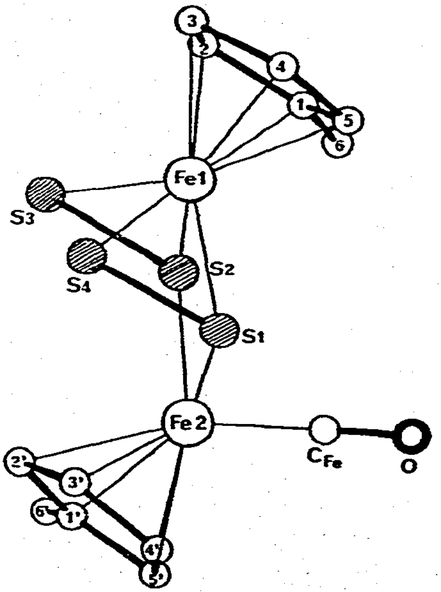

Fig. 1. A perspective view of the molecule. Only one statistical position of the disordered methylcyclopentadienyl is shown for clarity.

TABLE 1

FRACTIONAL ATOMIC COORDINATES (X10⁴) AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(β_{ij} (values X10⁴) are anisotropic coefficients in the expression: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; B is the isotropic thermal factor in Å^2.)

Atom	x	y	z	B or β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe(1)	6636(2)	8109(2)	6009(1)	30(3)	41(2)	19(1)	−3(3)	1(2)	−2(1)
Fe(2)	3501(3)	8812(2)	6414(1)	36(3)	86(3)	24(1)	14(3)	−4(2)	−6(1)
S(1)	5216(5)	9422(4)	5888(3)	76(7)	51(5)	21(2)	7(5)	−5(3)	5(2)
S(2)	5005(4)	7631(4)	6618(2)	51(6)	66(5)	27(1)	−6(5)	2(3)	6(2)
S(3)	5358(5)	6698(4)	5966(3)	93(7)	38(5)	38(2)	−10(5)	1(4)	−5(3)
S(4)	5601(5)	8641(4)	5191(2)	105(7)	87(5)	15(1)	25(6)	−5(3)	−5(2)
C(Fe)	4018(21)	9500(16)	6984(10)	6.0(6)					
O	4311(14)	10030(11)	7330(7)	6.7(5)					
C(1)	8217(19)	7560(17)	6536(9)	4.1(5)					
C(2)	8485(17)	7324(13)	5935(7)	2.5(4)					
C(3)	8572(19)	8242(13)	5619(7)	3.4(4)					
C(4)	8357(21)	9027(15)	6021(9)	5.2(5)					
C(5)	8096(19)	8617(17)	6572(9)	4.0(6)					
C(6)	8068(17)	6716(14)	6982(8)	4.9(5)					
C′(1)	1870	7957	6218						
C′(2)	2196	8472	5711						
C′(3)	2074	9506	5817						
C′(4)	1631	9643	6370						
C′(5)	1481	8671	6628						
C′(6)	1975	6845	6317						
C″(1)	1939	8970	5890						
C″(2)	2176	7930	5859						
C″(3)	1855	7509	6393						
C″(4)	1475	8266	6760						
C″(5)	1536	9197	6451						
C″(6)	2036	9707	5405						

TABLE 2

BOND DISTANCES IN Å (e.s.d.'s) (S ··· S, Fe ··· Fe non-bonded atoms)

Fe(1) ··· Fe(2)	3.397(4)	Fe(2)—C′(1)	2.04
Fe(1)—S(1)	2.273(6)	Fe(2)—C′(2)	2.15
Fe(1)—S(2)	2.257(6)	Fe(2)—C′(3)	2.20
Fe(1)—S(3)	2.280(6)	Fe(2)—C′(4)	2.17
Fe(1)—S(4)	2.293(6)	Fe(2)—C′(5)	2.08
Fe(2)—S(1)	2.260(6)	Fe(2)—C′(6)	3.05
Fe(2)—S(2)	2.230(6)	Fe(2)—C″(1)	2.00
Fe(2)—C_{Fe}	1.70 (2)	Fe(2)—C″(2)	2.20
C_{Fe}—O	1.12 (3)	Fe(2)—C″(3)	2.39
S(1) ··· S(2)	2.953(8)	Fe(2)—C″(4)	2.29
S(1)—S(4)	1.980(8)	Fe(2)—C″(5)	2.03
S(2)—S(3)	2.006(8)	Fe(2)—C″(6)	3.03
S(3) ··· S(4)	3.183(8)		
Fe(1)—C(1)	2.13 (2)	C(1)—C(2)	1.47(3)
Fe(1)—C(2)	2.13(2)	C(1)—C(5)	1.42(3)
Fe(1)—C(3)	2.14(2)	C(1)—C(6)	1.55(3)
Fe(1)—C(4)	2.11(2)	C(2)—C(3)	1.44(2)
Fe(1)—C(5)	2.08(2)	C(3)—C(4)	1.43(3)
Fe(1)—C(6)	3.27(2)	C(4)—C(5)	1.43(3)

TABLE 3

VALENCE ANGLES IN DEGREES (e.s.d. 's) (S ··· S non-bonded atoms)

S(1)—Fe(1)—S(2)	81.4(3)	Fe(2)—S(2)—S(3)	113.3(3)
S(1)—Fe(1)—S(3)	106.7(3)	S(1) ··· S(2)—S(3)	92.9(3)
S(1)—Fe(1)—S(4)	51.4(3)	Fe(1)—S(3)—S(2)	63.2(3)
S(2)—Fe(1)—S(3)	52.5(3)	Fe(1)—S(3) ··· S(4)	46.1(3)
S(2)—Fe(1)—S(4)	107.2(3)	S(2)—S(3) ··· S(4)	86.6(3)
S(3)—Fe(1)—S(4)	88.2(3)	Fe(1)—S(4)—S(1)	63.8(3)
S(1)—Fe(2)—S(2)	82.3(3)	Fe(1)—S(4) ··· S(3)	45.7(3)
S(1)—Fe(2)—C(Fe)	90.3(3)	S(1)—S(4) ··· S(3)	86.8(3)
S(2)—Fe(2)—C(Fe)	90.8(3)	Fe(2)—C_{Fe}—O	173(2)
Fe(1)—S(1)—Fe(2)	97.1(3)	C(2)—C(1)—C(5)	107(2)
Fe(2)—S(1) ··· S(2)	48.4(3)	C(2)—C(1)—C(6)	121(2)
Fe(2)—S(1)—S(4)	114.1(3)	C(5)—C(1)—C(6)	133(2)
S(2) ··· S(1)—S(4)	93.8(3)	C(1)—C(2)—C(3)	109(2)
Fe(1)—S(2)—Fe(2)	98.4(3)	C(2)—C(3)—C(4)	106(2)
Fe(1)—S(2)—S(3)	64.3(3)	C(3)—C(4)—C(5)	110(2)
Fe(2)—S(2) ··· S(1)	49.3(3)	C(1)—C(5)—C(4)	108(2)

2.266(21) Å, and appear to be equivalent. The four sulfur atoms are coplanar within 0.005 Å. The Fe atoms are respectively 1.352 [Fe(1)] above and 1.480 Å [Fe(2)] below this plane. The two S—S bonds S(1)—S(4) 1.980(8) and S(2)—S(3) 2.006(8) Å with an average value of 1.993(8) Å] are shorter than the normal

TABLE 4

PRINCIPAL LEAST-SQUARES PLANES

Equations of the planes: $lx + my + nz + p = 0$; x, y and z are orthogonal coordinates in Å along the *a*, *b* and *c* axes.

Plane A (S(1)—S(2)—S(3)—S(4)]	$0.9800\,x + 0.0478\,y + 0.1931\,z - 8.3684 = 0$
Plane B[C(1) ··· C(5)]	$0.9806\,x + 0.0468\,y + 0.1903\,z - 11.4026 = 0$
Plane C[C'(1) ··· C'(5)]	$0.9494\,x + 0.0450\,y + 0.3107\,z - 6.7676 = 0$
Plane D[C''(1) ··· C''(6)]	$0.9516\,x + 0.1254\,y + 0.2804\,z - 7.2352 = 0$
Plane E[(A), (B), Fe(1), Fe(2)]	$0.0732\,x + 0.8192\,y - 0.5688\,z - 1.3576 = 0$

(A) and (B) being the midpoints of S(1) ··· S(2) and S(3) ··· S(4) and (C) the centre of the cyclopentadienyl linked to Fe(1).

Deviations (in Å) of atoms from these planes (*: atom included in the plane calculation)

	A	B	C	D	E	
Fe(1)	1.352(2)	−1.728(2)	4.380	4.371	−0.007(3) *	Fe(1)
Fe(2)	−1.480(3)	−4.566(3)	1.752	1.784	−0.006(3) *	Fe(2)
S(1)	−0.005(5) *	−3.088(5)	3.027	3.165	0.012 *	(A)
S(2)	0.005(5) *	−3.080(4)	3.252	3.145	0.001 *	(B)
S(3)	−0.005(5) *	−3.084(5)	3.054	2.894	−0.004	(C)
S(4)	0.005(5) *	−3.071(5)	2.836	2.941	0.025(22)	C(Fe)
C(1)	0.02(2) *	0.02(2) *			0.165(15)	O
C(2)		−0.01(2) *				
C(3)		−0.01(2) *				
C(4)		0.01(2) *				
C(5)		−0.02(2) *				
C(6)		0.02(2)				

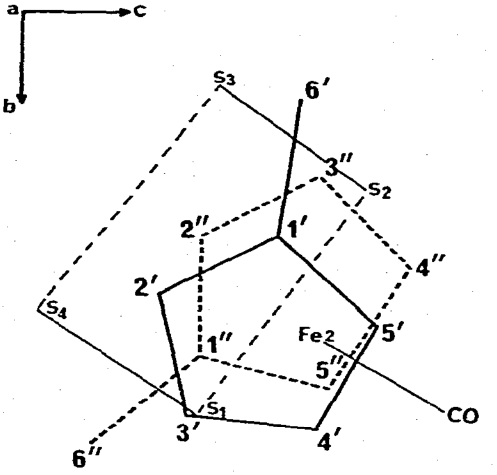

Fig. 2. Projection along the *a* axis illustrating the disorder of the methylcyclopentadienyl linked to Fe(2).

S—S bond of 2.06 Å [15]. The methylcyclopentadienyl linked to Fe(1) is planar with a mean value of 1.44(3) Å for the C—C bonds and 108(2)° for the internal angles. It is interesting to note that the molecule has an overall C_s symmetry, the plane of symmetry passing through the Fe(1) and Fe(2) atoms, the carbonyl group, the midpoints of S(1)···S(2) and S(3)···S(4) and the centre of the methylcyclopentadienyl linked to Fe(1), as shown in Table 4. In the crystal, the methylcyclopentadienyl linked to Fe(2) appears to be disordered. The two statistical orientations, illustrated in Fig. 2 as obtained from the refinement, are symmetrical with respect to this approximate plane of symmetry. The dihedral angle between these two positions is 5.5°. Distances between statistical atoms are given in Table 5.

Experimental

The IR spectra were taken in solution (4000—625 cm^{-1}), with KBr disc (4000—250 cm^{-1}) and in polythene (400—40 cm^{-1}), respectively, on Perkin—Elmer 257, 357 and Beckman RIIC FS 720 Interferometer Model Instruments, the ^1H and ^{13}C NMR spectra were taken in $CDCl_3$ or toluene solution on Varian T60, A60A and Bruker WP60 model instruments respectively, with tetramethylsilane as internal reference, and the mass spectra on an AEI MS9 instrument.

TABLE 5

SHORTEST DISTANCES (Å) BETWEEN THE TWO ORIENTATIONS OF THE DISORDERED METHYLCYCLOPENTADIENYL RING

C′(1) — C″(2)	0.90	C′(3) ··· C″(1)	0.75
C′(1) ··· C″(3)	0.73	C′(4) ··· C″(5)	0.63
C′(2) ··· C″(2)	0.80	C′(5) ··· C″(4)	0.62
C′(2) ··· C″(1)	0.83	C′(5) — C″(5)	0.82

We used GF 254 (Merck) silicagel for the thin-layer chromatographic separation and $CHCl_3$ for elution.

General photolysis

To a 2 dm^3 of well-deoxygenated saturated methanol solution of cyclooctasulfur we add 1.5×10^{-3} *M* of purified cyclopentadienyliron carbonyl dimer derivatives (from Alfa). The mixture is irradiated with visible light from an OSRAM Model X BF-Xe 2.5 kW arc lamp with copper sulfate solution as filter [16]. After the irradiation the solution is deep green. The solvent is removed under vacuum. The green mixture is chromatographed on a thin-layer apparatus to give a large green band (R_f 0.7). The yield of the green powder is about 35%. The compound is characterised by its elemental analysis and its ^1H and ^{13}C NMR and IR spectra.

Photolysis of cyclopentadienyliron carbonyl dimer

When the photolysis is carried out with cyclopentadienyliron carbonyl dimer we obtain a mixture of the corresponding bis(cyclopentadienyliron)monocarbonyl tetrasulfide; elemental analysis: Found: C, 33.22; H, 2.54; S, 30.13. $C_{11}H_{10}Fe_2S_4O$ calcd.: C, 33.16; H, 2.51; S, 32.16%. ^{13}C NMR ($CHCl_3$) δ(ppm): CO 83.38 (s), π^5-C_5H_5 86.69 (s). ^1H NMR δ (ppm) π^5-C_5H_5 large (m) centered at 4.60.

Photolysis of methylcyclopentadienyliron carbonyl dimer

The photolysis was carried out as described above. Elemental analysis: Found: C, 36.78; H, 2.51; S, 28.37. $C_{13}H_{14}Fe_2OS_4$ calcd.: C, 36.62; H, 3.28; S, 30.04%. ^{13}C NMR δ (ppm): CH_3 12.081 (s); CO 85.967 (s); π-C_5H_4 86.45, 86.75, 87.24 (m). ^1H NMR δ (ppm): CH_3 1.6 (m), π-C_5H_5 2 (m) centered at 4.2.

X-Ray methods

The crytal data are: $C_{13}H_{14}Fe_2OS_4$, mol. wt. 426, orthorhombic space group *Pbca*, cell dimensions: *a* 9.964(6), *b* 13.346(26), *c* 23.470(24) Å, *V* 3121 Å^3, eight molecules in the unit cell ($Z = 8$), $D_c = 1.81$, λ(Mo-K_α) 0.7107 Å.

The intensities were measured with graphite monochromated Mo-K_α radiation on a PW 1100 diffractometer using the $\theta - 2\theta$ scan. Cell constants were obtained by least-squares refinement of the setting angles of 20 reflexions. Of the 2229 collected reflexions only 859 having $I > 2.0\ \sigma(I)$, $\sigma(I)$ being the standard deviation derived from counting statistics, were used for the structure analysis. The intensities were corrected for Lorentz and polarisation effects but not for absorption.

Scattering factors were taken from the International Tables for X-Ray Crystallography (1974) [17]. A three-dimensional Patterson synthesis yielded the position of the two iron atoms. Five successive Fourier syntheses gave the location of all the non-hydrogen atoms, but the cyclopentadienyl ligand linked to Fe(2) was found to be disordered. Full-matrix least-squares refinement was followed by a difference Fourier synthesis, which clearly revealed the presence of two methyl groups for the disordered methyl cyclopentadienyl ring along with unresolved positions for the ring atoms. Therefore in subsequent refinements (program ORION [18]) this ring was treated as a rigid group with two equally weighted orientations and having the same dimensions as those in a (π^5-methylcyclopentadienyl)cobalt−iron complex [18]. The temperature factors were anisotropic for the Fe and S atoms, and isotropic for C and O: those of the rigid groups were fixed ($B = 5$ Å^2).

The function minimized was $\Sigma w(F_0 - F_c)^2$ where $w = 1/\sigma(F_0)^2$. The final R factors were 0.08 and $R_w = 0.07$ *.

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* Tables of structure factors may be obtained from the authors.