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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.032
 wR factor = 0.088
Data-to-parameter ratio = 17.8For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Hexacarbonylbis(μ_2 -2-methoxyphenyl-
thiolato)diiron(I)(Fe—Fe)

In the title compound, $[\text{Fe}_2(\text{CO})_6(\text{C}_7\text{H}_7\text{OS})_2]$ or $[\text{Fe}_2(\text{SPh-2-OMe})_2(\text{CO})_6]$, each Fe atom is coordinated by three terminal carbonyl C atoms [$\text{Fe}-\text{C}$ 1.779 (2)–1.819 (2) Å], two bridging S atoms [$\text{Fe}-\text{S}$ 2.2747 (7)–2.2933 (7) Å] and the other Fe atom [$\text{Fe}-\text{Fe}$ 2.4979 (5) Å], displaying a highly distorted octahedral geometry with *cis* angles ranging from 74.59 (3) to 105.88 (7)°.

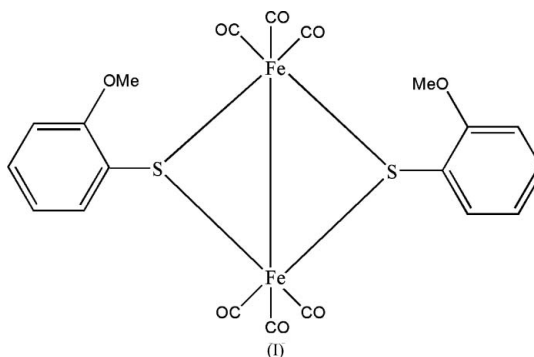
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Comment

Hydrogenases are enzymes that catalyse the reversible two-electron oxidation of H_2 (Marr *et al.*, 2001). It is well established that the Fe-only hydrogenases have an Fe_2S_2 core that is the active site. Crystallography revealed that this active site is cysteine-S bridged to an Fe_4S_4 cluster, the first in a series of Fe–S clusters that form the electron-transport route to biological electron donor/acceptor sites. The two Fe atoms are, in fact, bridged together, by two non-protein thiolates or sulfides, and other coordination sites are occupied by diatomic ligands which have been identified to be CO and CN^- (Pierik *et al.*, 1999). The title compound, (I), exhibits some resemblance to the active site of Fe-hydrogenases.



As shown in Fig. 1, compound (I) contains two $\text{Fe}(\text{CO})_3$ subunits which are bridged by two thiolate ligands, resulting in an Fe_2S_2 core. This Fe_2S_2 core displays the well known butterfly arrangement, with a dihedral angle of 93.0 (2)° between the two Fe~2~S planes. The average Fe–S distance [2.282 (8) Å] compares well with those found in other similar complexes (Ashby, 1995). The Fe–Fe distance in (I) is shorter than that reported in $[\text{Fe}_2(\text{SPh-4-OH})_2(\text{CO})_6]$ [2.522 (1) Å; Ashby, 1995].

An octahedral environment around each metal centre in (I) is completed through the additional coordination of three terminal carbonyl groups. The octahedra are distorted, as indicated by the *trans* angles, which vary from 149.25 (7) to 159.47 (7)°. The average Fe–C distance [1.797 (5) Å] in (I) is longer than that found in $[\text{Fe}_2(\text{SPh-4-OH})_2(\text{CO})_6]$

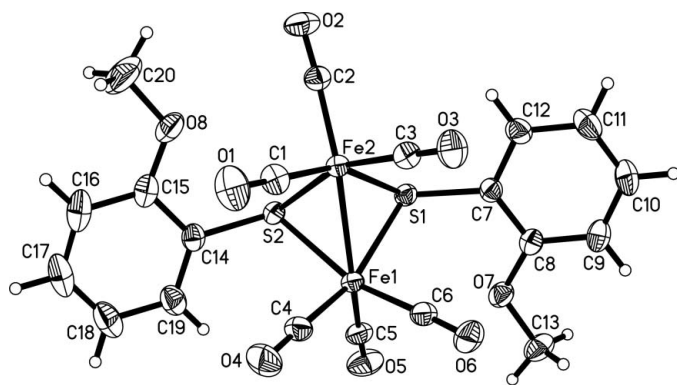


Figure 1
A drawing of the title compound, with the atomic labelling scheme and 30% probability displacement ellipsoids.

[1.789 (15) Å; Ashby, 1995] and the average Fe—S—Fe angle [66.357 (16)°] in (I) is slightly smaller than that observed in [Fe₂(SPh-4-OH)₂(CO)₆] [67.6 (4)°; Ashby, 1995].

Experimental

The synthesis was carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. Fe₃(CO)₁₂ (1.0 g, 1.98 mmol) was dissolved in dry tetrahydrofuran (40 ml) under a nitrogen atmosphere and then 2-methoxythiophenol (0.5 ml, 4 mmol) was added. The mixture was refluxed for 2 h, which resulted in the formation of a dark-red solution. This dark-red solution was allowed to cool to room temperature and the majority of the solvent was evaporated *in vacuo*. The remaining solution was filtered through silica gel. A dark-red fraction was collected by elution with hexane. Recrystallization of the crude product from distilled hexane in a fridge for 2 d gave the title compound, (I), as dark-red crystals (670 mg, 40% yield).

Crystal data

[Fe ₂ (CO) ₆ (C ₇ H ₇ OS) ₂]	Mo K α radiation
$M_r = 558.13$	Cell parameters from 8106 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 3.0\text{--}27.5^\circ$
$a = 14.206$ (4) Å	$\mu = 1.52$ mm ⁻¹
$b = 14.015$ (4) Å	$T = 298$ K
$c = 22.639$ (6) Å	Prism, dark red
$V = 4507$ (2) Å ³	0.55 × 0.50 × 0.40 mm
$Z = 8$	
$D_x = 1.645$ Mg m ⁻³	

Data collection

Rigaku Mercury CCD area-detector diffractometer	5148 independent reflections
ω scans	4915 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.452$, $T_{\text{max}} = 0.549$	$\theta_{\text{max}} = 27.5^\circ$
32701 measured reflections	$h = -18 \rightarrow 18$
	$k = -17 \rightarrow 18$
	$l = -17 \rightarrow 29$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.8475P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.46$ e Å ⁻³
5148 reflections	$\Delta\rho_{\text{min}} = -0.21$ e Å ⁻³
289 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Fe1—C4	1.784 (2)	Fe2—C1	1.779 (2)
Fe1—C6	1.786 (2)	Fe2—C3	1.798 (2)
Fe1—C5	1.819 (2)	Fe2—C2	1.819 (2)
Fe1—S1	2.2747 (7)	Fe2—S2	2.2808 (7)
Fe1—S2	2.2803 (7)	Fe2—S1	2.2933 (7)
Fe1—Fe2	2.4979 (5)		
C4—Fe1—C6	87.98 (10)	C1—Fe2—C3	90.82 (10)
C4—Fe1—C5	103.49 (11)	C1—Fe2—C2	95.98 (10)
C6—Fe1—C5	98.19 (10)	C3—Fe2—C2	99.31 (10)
C4—Fe1—S1	156.69 (8)	C1—Fe2—S2	93.25 (8)
C6—Fe1—S1	94.66 (7)	C3—Fe2—S2	159.78 (7)
C5—Fe1—S1	99.05 (8)	C2—Fe2—S2	99.95 (7)
C4—Fe1—S2	94.85 (7)	C1—Fe2—S1	156.41 (8)
C6—Fe1—S2	159.47 (7)	C3—Fe2—S1	94.23 (7)
C5—Fe1—S2	100.89 (7)	C2—Fe2—S1	105.88 (7)
S1—Fe1—S2	74.96 (2)	S2—Fe2—S1	74.59 (3)

H atoms were positioned geometrically and allowed to ride on their parent atoms, with CH₃ and aromatic CH bonds set to 0.96 and 0.93 Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic CH and $1.5U_{\text{eq}}(\text{C})$ for CH₃.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Siemens, 1994); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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