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μ_4-Sulfido-bis(μ_2-phenylthiolato)tetrakis(tricarbonyliron)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.016 Å
R factor = 0.069
wR factor = 0.147
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title complex, $C_{24}H_{10}Fe_4O_{12}S_3$, contains two $Fe_2(PhS)(CO)_6$ subclusters connected through an inorganic spiro μ_4-S atom. Each iron atom is coordinated by three carbonyl C atoms [Fe—C 1.786 (9)–1.826 (9) Å], one thiophenyl S atom [Fe—S 2.267 (2)–2.286 (2) Å], one μ_4–S atom [Fe—S 2.235 (2)–2.249 (2) Å], and one Fe—Fe bond [2.526 (16), 2.532 (16) Å], in a distorted octahedral geometry.

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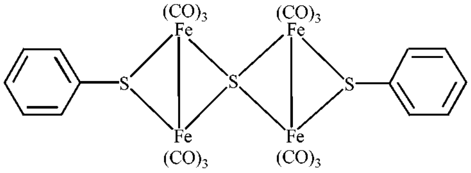
Comment

Hydrogenases are utilized by numerous microorganisms to process hydrogen, in both the production and the uptake of molecular hydrogen, in support of their metabolism. Fairly recently, crystallographic investigations of the so-called Fe-only hydrogenases discovered a six-iron H-cluster containing an $Fe_2(\mu\text{-}SR)_2(CN)_2(CO)_3L_n$ core [R is alkyl, L is H_2O], and a thiolate-linked $Fe_4S_4(SR)_4$ cluster. The metabolism of hydrogen is facilitated at a novel 2Fe2S center in Fe-only hydrogenase (Peters *et al.*, 1998; Nicolet *et al.*, 1999; Nicolet *et al.*, 2001). To simulate the organometallic structure $Fe_2(SR)_2(CN)_2(CO)_4$ of the H-cluster, we repeated the preparation of $Fe_2(SR)_2(CO)_6$ by the reaction of $Fe_3(CO)_{12}$ with thiophenol, using the method of Rauchfuss (Gloaguen *et al.*, 2001). We obtained the title compound, (I), which represents a new example of an Fe_4S_3 core cluster containing a bridging thiophenyl ligand. However, similar structures have been reported in other complexes, *viz.* $[CH_3SFe_2(CO)_6]_2S$ (Coleman *et al.*, 1967), $[C_6H_9SFe_2(CO)_6]_2S$ (Kolobkov *et al.*, 1986), and $[EtSFe_2(CO)_6]_2S$ (Song *et al.*, 1988).



(I)

Complex (I) contains two $Fe_2S(CO)_6$ subclusters Fe1,S2,Fe2 and Fe3,S3,Fe4, connected through the inorganic sulfur atom, μ_4-S1, as shown in Fig. 1. Each subcluster has a phenyl group, attached to μ_2-S2 and μ_2-S3, respectively. In each subcluster, two Fe atoms are bridged by the thiophenyl S, with an average Fe—S—Fe angle of 67.48 (7)° and an average Fe—S distance of 2.276 (2) Å. The Fe—Fe separations of 2.526 (16) and 2.532 (16) Å are comparable to those in the H-cluster. The central S atom, S1, connects the two $Fe_2S(CO)_6$ fragments, with a shorter Fe—S distance, averaging 2.243 (2) Å. The Fe—S1—Fe angles, ranging from 68.44 (7)° to 138.97 (10)°, show that the Fe_4S tetrahedron is very distorted. In addition to the coordination of one thiophenyl S and one μ_4-S, the 18-elec-

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tron shell of each Fe atom is completed by three terminal carbonyl groups, with an average Fe—C bond length of 1.800 (10) Å.

Experimental

Reactions were carried out under an atmosphere of purified nitrogen, using standard Schlenk techniques. To 1 g $Fe_3(CO)_{12}$ suspended in 40 ml toluene was added 2 equiv. of thiophenol. The solution changed from black–green to black–red after stirring for 1 h. Stirring was continued, at 343 K, overnight; the solution was then cooled to room temperature, filtered and evaporated to dryness *in vacuo*. The residue was extracted with 3 × 10 ml hexane, and the combined extracts were reduced to *ca.* 5 ml *in vacuo*, yielding a red crystal of (I), at 253 K.

Crystal data

$[Fe_4C_{24}H_{10}O_{12}S_3]$
$M_r = 809.90$
Monoclinic, $P2_1/n$
$a = 9.0026$ (2) Å
$b = 12.9509$ (4) Å
$c = 26.5409$ (2) Å
$\beta = 97.612$ (1)°
$V = 3067.18$ (12) Å^3
$Z = 4$
$D_x = 1.754$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4211 reflections
$\theta = 2.2$–25.1°
$\mu = 2.12$ mm^{-1}
$T = 293$ (2) K
Prism, red
0.50 × 0.38 × 0.36 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.326$, $T_{\max} = 0.467$
9335 measured reflections
5418 independent reflections
4103 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 25.1°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 15$
$l = -31 \rightarrow 17$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.147$
$S = 1.03$
5418 reflections
388 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0017P)^2 + 30.5273P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.41$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—C3	1.791 (8)	Fe3—C7	1.786 (9)
Fe1—C1	1.790 (9)	Fe3—C8	1.798 (9)
Fe1—C2	1.820 (10)	Fe3—C9	1.802 (9)
Fe1—S1	2.249 (2)	Fe3—S1	2.244 (2)
Fe1—S2	2.281 (2)	Fe3—S3	2.286 (2)
Fe1—Fe2	2.5256 (16)	Fe3—Fe4	2.5313 (16)
Fe2—C4	1.796 (10)	Fe4—C12	1.793 (10)
Fe2—C5	1.803 (10)	Fe4—C10	1.787 (10)
Fe2—C6	1.826 (9)	Fe4—C11	1.810 (11)
Fe2—S1	2.243 (2)	Fe4—S1	2.235 (2)
Fe2—S2	2.267 (2)	Fe4—S3	2.270 (2)
Fe4—S1—Fe2	131.96 (10)	Fe2—S1—Fe1	68.43 (7)
Fe4—S1—Fe3	68.81 (7)	Fe3—S1—Fe1	125.67 (9)
Fe2—S1—Fe3	135.79 (10)	Fe2—S2—Fe1	67.46 (7)
Fe4—S1—Fe1	138.98 (10)	Fe4—S3—Fe3	67.51 (7)

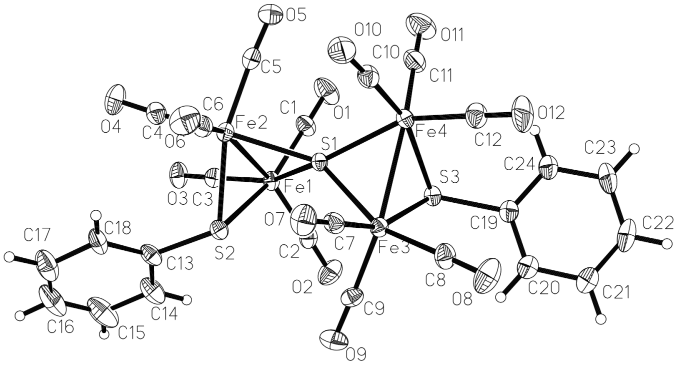

Figure 1
Molecular structure of the title compound, with the atom-labeling scheme and probability displacement ellipsoids drawn at the 30% level.

H atoms bonded to C were placed in calculated positions, with C—H distances of 0.93 Å, and treated as riding atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT* and *XPREP* in *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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