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Hexacarbonylhexakis(μ-3,4-dimethylbenzenethiolato)triiron(II)

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The title complex, $[Fe_3(C_8H_9S)_6(CO)_6]$, contains one Fe^{II} atom and two $Fe(CO)_3$ subclusters connected through six 3,4-dimethylbenzenethiolate (μ_2-S) ligands. The compound crystallizes in the trigonal space group $R\overline{3}$ with two independent molecules in the asymmetric unit, one molecule possessing an inversion center and the other possessing $\overline{3}$ symmetry. The Fe—S bond lengths are in the range 2.3386 (9)–2.5733 (8) Å and the S—Fe—S angles are in the range 81.20 (3)–83.74 (3)°.

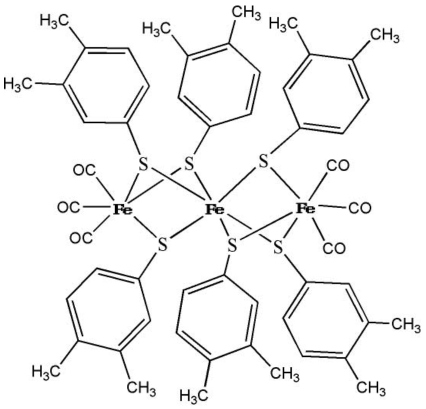
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.006 Å
R factor = 0.049
wR factor = 0.106
Data-to-parameter ratio = 15.7

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

Comment

Hydrogenases are highly efficient hydrogen-processing enzymes present in microorganisms for both the production and the uptake of dihydrogen. In the two major types of organometallic hydrogenases, all iron hydrogenases are more O_2-sensitive than [NiFe] hydrogenases and are more efficient for H_2 production (Adams, 1990). X-ray crystallographic studies for Fe-only hydrogenases on the H_2-uptake enzyme from *D. desulfuricans* and the H_2-evolving enzyme from *C. pasteurianum* have recently shown that the H-cluster (hydrogen-producing cluster) is actually composed of a binuclear iron unit, *viz.* (μ-SRS)$[Fe(CO)_2L]_2$ (with R = alkyl, L = cyano or hydride), and a typical [$4Fe_4S$] cluster bridged through a cysteine-S residue to each other (Peters *et al.*, 1998; Nicolet *et al.*, 1999, 2001). Encouraged by the details revealed by high-resolution protein crystallography, new biologically relevant structures, simulating the organometallic structure $Fe_2(SR)_2(CN)_2(CO)_4$ of the H-cluster, have been proposed. We repeated the preparation of $Fe_2(SR)_2(CO)_6$ by the reaction of $Fe_3(CO)_{12}$ with the arenethiol species, using the method of Rauchfuss (Gloaguen *et al.*, 2001).



(I)

We obtained the title compound, (I), which represents a new example of a [3Fe6S] core cluster containing bridging arenethiolate ligands. Similar clusters have been reported in

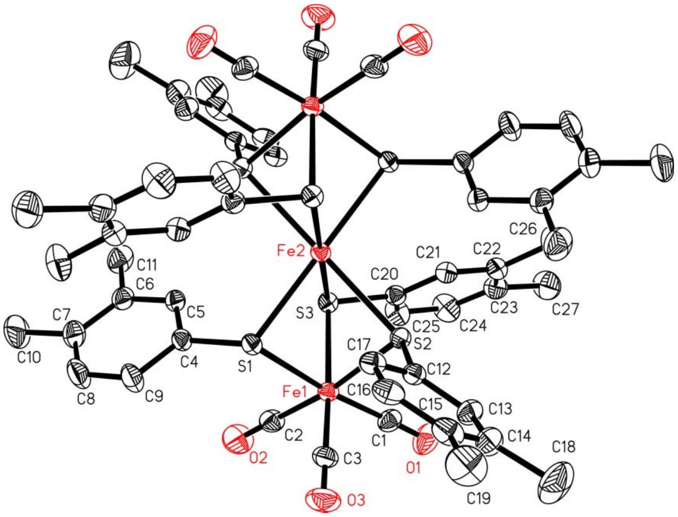


Figure 1

A view of the molecular structure of the triiron cluster in (I), which possesses an inversion center (atom Fe2). Unlabeled atoms are related to labeled atoms by $(1 - x, -y, -z)$. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

other complexes, *e.g.* $Fe_3(CO)_6(C_6H_5S)_6$ (Berger & Strahle, 1984; Walters & Dewan, 1986).

Complex (I) crystallizes in a solvent-free form in the trigonal space group $R\overline{3}$, with parts of two independent neutral linear triiron clusters per asymmetric unit. The molecular structure of the triiron cluster possessing an inversion center (atom Fe2) is shown in Fig. 1. The molecular structure of the triiron cluster possessing $\overline{3}$ symmetry (atom Fe4) is shown in Fig. 2. Each Fe atom has an 18-electron shell attributed to four electrons of μ_2–S and two electrons of the terminal carbonyl groups. The central Fe^{II} atoms are bridged to two outer symmetrical $Fe(CO)_3$ subclusters through six dimethylbenzenethiolate ligands, with the $Fe_{central}—S$ distances ranging from 2.4726 (8) to 2.5733 (8) Å and the $Fe_{central}—S—Fe_{carbonyl}$ angles ranging from 81.20 (3) to 83.74 (3)°. The $Fe(CO)_3$ subcluster has an octahedral coordination and is comparable in size to that of the organometallic model complexes for the H-cluster. The average $Fe_{carbonyl}—S$ and $Fe_{carbonyl}—C$ distances of 2.3473 (5) and 1.803 (2) Å, respectively, fall within the range of those from the binuclear organometallic models, *e.g.* $(SCH_2C_6H_4CH_2S)Fe_2(CO)_6$ (Lyon *et al.*, 2001), $(SC_6H_5)_2Fe_2(CO)_6$ (Adeleke *et al.*, 1992).

Experimental

Reactions were carried out under an atmosphere of purified nitrogen, using standard Schlenk techniques. $Fe_3(CO)_{12}$ (1 g) was suspended in tetrahydrofuran (4 ml), followed by the addition of 2 equivalents of 3,4-dimethylbenzenethiol. The solution changed from very dark green to very dark red after stirring for 1 h. Stirring at 343 K was continued overnight, after which the solution was cooled to room temperature, filtered and evaporated to dryness in a vacuum. The residue was extracted with hexane (3 × 10 ml), and the combined extracts were then reduced to *ca* 5 ml in a vacuum. Red crystals of (I) were obtained from this solution at 253 K.

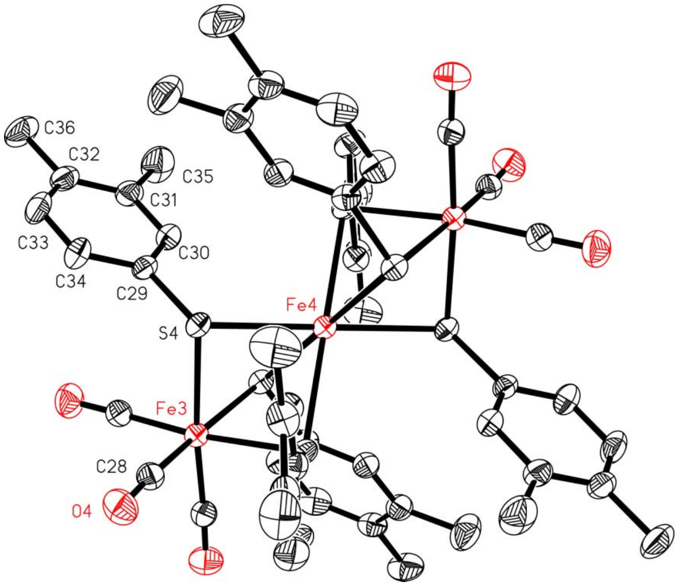


Figure 2

A view of the molecular structure of the triiron cluster in (I), which possesses $\overline{3}$ symmetry (atom Fe4). Unlabeled atoms are related to labeled atoms by threefold inversion symmetry. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Crystal data

$[Fe_3(C_8H_9S)_6(CO)_6]$
$M_r = 1158.88$
Trigonal, $R\overline{3}$
$a = 40.0008$ (12) Å
$c = 12.0928$ (6) Å
$V = 16756.9$ (7) Å^3
$Z = 12$
$D_x = 1.378$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10 404 reflections
$\theta = 1.8$–25.0°
$\mu = 1.04$ mm^{-1}
$T = 293$ (2) K
Prism, black
0.50 × 0.30 × 0.15 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.695$, $T_{max} = 0.856$
34 520 measured reflections
6567 independent reflections
5848 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 25.0°$
$h = -47 \rightarrow 44$
$k = -47 \rightarrow 47$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.106$
$S = 1.09$
6567 reflections
417 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2 + 59.4153P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.31$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

H atoms were placed in calculated positions and treated as riding atoms, with C—H distances of 0.93 Å and with $U_{iso}(H) = 1.2U_{eq}(C)$.

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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