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(μ_4-Disulfido-1:2κ^2S,S;3:4κ^2S',S')bis(μ_2-ethylthiolato-$\kappa^2S:S$)tetrakis[tricarbonyliron(II)(Fe—Fe)]

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Key indicators

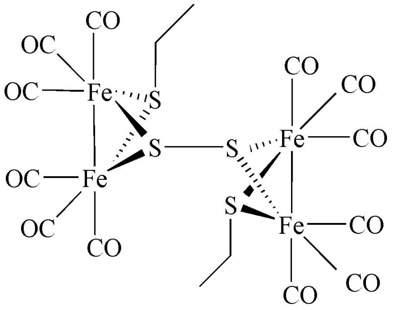
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.006 Å
R factor = 0.040
wR factor = 0.094
Data-to-parameter ratio = 18.8

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

The title compound, [$Fe_4(SEt)_2(S_2)(CO)_{12}$], contains two inversion-related [$Fe_2(SEt)(CO)_6$] subclusters linked by a disulfide bond [S—S 2.1294 (14) Å]. In each subcluster, each Fe^{II} atom is coordinated by three terminal carbonyl C atoms [Fe—C 1.792 (3)–1.814 (4) Å], two bridging S atoms [Fe—S 2.2496 (9)–2.2606 (8) Å] and the other Fe atom [Fe—Fe = 2.5311 (7) Å], and exhibits a distorted octahedral geometry, with *trans* angles ranging from 155.56 (12) to 160.14 (15)°.

Comment

Modelling studies of Fe-only hydrogenase (H-cluster) have attracted considerable attention due to the high efficiency of the compound in the process of oxidation of dihydrogen and the reverse reaction, and the formation of molecular hydrogen from protons (Florin *et al.*, 2001). Numerous previous studies have shown that the main active centre is based on a 2Fe–2S butterfly structure, while the 4Fe–4S cubane cluster only functions as the pathway for electron transfer. The two subunits are connected by a cysteine-S atom (Salyi *et al.*, 2003; Nicolet *et al.*, 1999, 2001). Therefore, much current work focuses on the preparation of analogous $Fe_2(SCH_2)_2NR(CO)_6$ subunits and various similar clusters. In contrast with the previous synthetic reaction of $(ClCH_2)_2NR$ with $Li_2[Fe_2(S_2)(CO)_6]$ (Lawrence *et al.*, 2001), we tried a new approach involving the condensation of paraformaldehyde, amines and metal sulfides $Fe_2(SH)_2(CO)_6$ (Li & Thomas, 2002), and obtained the title compound, (I), which represents a new example of Fe_4S_4 core clusters involving a relatively rare μ_4-S—S bridging ligand (Seyferth *et al.*, 1985; Bose *et al.*, 1984). We report here the synthesis and single-crystal structure of (I).



(I)

As shown in Fig. 1, the molecule of (I) sits on a crystallographically imposed centre of inversion at the mid-point of the disulfide bond, and the asymmetric unit thus contains one-half of the [$Fe_4(SEt)_2(S_2)(CO)_{12}$] formula unit. The two inversion-related pairs of Fe atoms are each bridged by a

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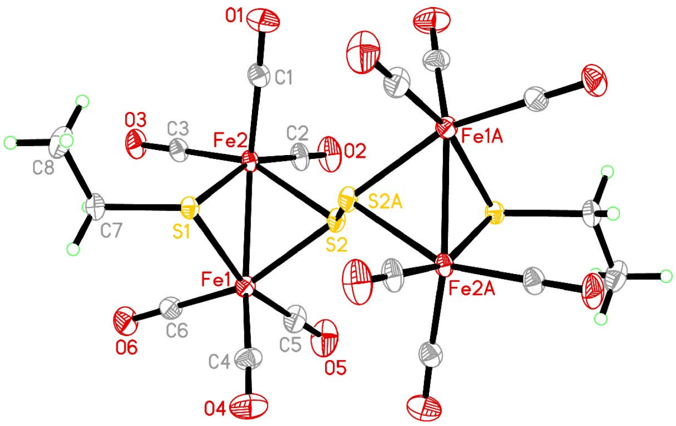

Figure 1
The molecular structure of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix A are at the symmetry position $(1-x, 1-y, -z)$.

thiolato group (μ-SEt) and an inorganic S atom (μ-S_2). As listed in Table 1, the average Fe—S distance [2.2552 (9) Å] and the average Fe—S—Fe angle [68.32 (3)°], as well as the Fe—Fe distance [2.5311 (7) Å], are comparable with those found in the tetranuclear complex $[Fe_4(\mu\text{-SEt})_2(\mu_4\text{-S})(CO)_{12}]$ [2.256 (2) Å, 68.50 (8)° and 2.542 (2) Å, respectively; Song *et al.*, 1988]. An octahedral arrangement around each Fe centre is completed through the additional coordination of three terminal carbonyl groups, with the Fe—C bond distances averaging 1.800 (4) Å, and the octahedra are highly distorted, as indicated by the *cis* angles varying from 81.65 (3) to 105.25 (12)°.

Each of the symmetry-related $[Fe_2(\mu\text{-SEt})(\mu\text{-S})]$ cores displays a 'butterfly' arrangement, with a dihedral angle of 104.5 (2)° between the Fe_2S planes. The two $[Fe_2(\mu\text{-SEt})(CO)_6]$ subclusters in (I) are coupled by an S—S bond [S2—S2A 2.1294 (14) Å]. The S—S bond is lengthened relative to the single S—S bond in elemental sulfur [2.037 (5) Å; Anderson *et al.*, 1980]. The rare bridging Fe_2—S—S—Fe_2 structural unit is also found in a similar tetranuclear complex, $[\{Fe_2(\mu\text{-SPh})(CO)_6\}_2(\mu\text{-}S_2)]$ (Seyferth *et al.*, 1985), which has shorter Fe—Fe [2.525 (2) Å] and S—S [2.106 (3) Å] bonds than (I), probably due to the larger substituent attached to the S atom in the latter.

Two substituent ethyl groups are linked to atoms S1 and S1*A* by an equatorial type of bond, the S—C bond length being 1.823 (3) Å. Besides the coordination of one ethylthiolate S and one inorganic S, the 18-electron shell of each Fe atom is completed by three terminal carbonyl groups and the other Fe atom.

The packing diagram (Fig. 2) shows a layer-type arrangement, with parallel stacks of molecules of (I) along the *c* axis. The complete solid-state structure is stabilized by van der Waals interactions.

Experimental

Reactions were carried out in an atmosphere of purified nitrogen using standard Schlenk techniques. A solution of paraformaldehyde (1.2 g, 4 mmol) and 4-$CNC_6H_4NH_2$(2.37 g, 2 mmol) in tetrahydrofuran (20 ml) was stirred for 6 h. The resulting suspension was treated with $Fe_2(SH)_2(CO)_6$ (1 mmol) at 273 K with stirring for an additional 1 h, then cooled to room temperature. The resulting red solution was filtered and evaporated to dryness *in vacuo*, and the residue was recrystallized from CH_2Cl_2 at 253 K, yielding red crystals of (I).

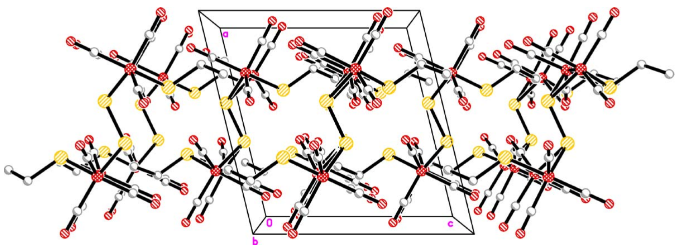

Figure 2
A packing diagram for (I), viewed along the *b* axis. H atoms have been omitted for clarity.

Crystal data

$[Fe_4(C_2H_5)_2(S_2)(CO)_{12}]$
$M_r = 745.88$
Monoclinic, $P2_1/c$
$a = 10.4820$ (11) Å
$b = 13.1288$ (15) Å
$c = 10.0749$ (11) Å
$\beta = 103.719$ (4)°
$V = 1346.9$ (3) Å^3
$Z = 2$
$D_x = 1.839$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2637 reflections
$\theta = 3.1$–$27.5°$
$\mu = 2.48$ mm^{-1}
$T = 298$ (2) K
Prism, red
0.25 × 0.20 × 0.10 mm

Data collection

Rigaku Mercury CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.525$, $T_{max} = 0.781$
10 263 measured reflections
3070 independent reflections
2417 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 27.5°$
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 16$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.094$
$S = 1.06$
3070 reflections
163 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.0725P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—C6	1.797 (4)	Fe2—C3	1.792 (3)
Fe1—C5	1.798 (4)	Fe2—C2	1.797 (3)
Fe1—C4	1.804 (4)	Fe2—C1	1.814 (4)
Fe1—S2	2.2515 (9)	Fe2—S2	2.2496 (9)
Fe1—S1	2.2535 (8)	Fe2—S1	2.2606 (8)
Fe1—Fe2	2.5311 (7)		
C6—Fe1—C5	91.35 (16)	C3—Fe2—C2	90.59 (14)
C6—Fe1—C4	99.12 (17)	C3—Fe2—C1	99.40 (16)
C5—Fe1—C4	99.93 (19)	C2—Fe2—C1	100.86 (16)
C6—Fe1—S2	155.56 (12)	C3—Fe2—S2	155.83 (11)
C5—Fe1—S2	86.23 (13)	C2—Fe2—S2	86.31 (12)
C4—Fe1—S2	105.25 (12)	C1—Fe2—S2	104.73 (11)
C6—Fe1—S1	93.07 (11)	C3—Fe2—S1	93.74 (10)
C5—Fe1—S1	160.14 (15)	C2—Fe2—S1	159.73 (13)
C4—Fe1—S1	98.46 (12)	C1—Fe2—S1	97.94 (10)
S2—Fe1—S1	81.77 (3)	S2—Fe2—S1	81.65 (3)

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H atoms bonded to C atoms were placed in calculated positions, with C—H distances of 0.96 and 0.97 Å, and treated as riding atoms, with $U_{\rm iso}$(H) = 1.2 or 1.5$U_{\rm eq}$(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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References

Anderson, E. L., Fehlner, T. P., Foti, A. E. & Salahub, D. R. (1980). *J. Am. Chem. Soc.* **102**, 7422–7429.

Bose, K. S., Sinn, E. & Averill, B. A. (1984). *Organometallics*, **3**, 1126–1128.

Florin, L., Tsokoglou, A., & Happe, T. J. (2001). *J. Biol. Chem.* **276**, 6125–6132.

Lawrence, J. D., Li, H. & Rauchfuss, T. B. (2001). *Chem. Commun.* pp. 1482–1483.

Li, H. & Thomas, B. R. (2002). *J. Am. Chem. Soc.* **124**, 726–727.

Nicolet, Y., de Lacet, A. L., Vernede, X., Fernandez, V. M., Hatchikian, E. C. & Fontecilla-Camps, J. C. (2001). *J. Am. Chem. Soc.* **123**, 1596–1601.

Nicolet, Y., Pairas, C., Legrand, P., Hatchikian, E. C. & Fontecilla-Camps, J. C. (1999). *Structure*, **7**, 13–23.

Rigaku (2000). *CrystalClear*. Version 1.35. Rigaku Corporation, 3-9-12 Akishima Tokyo, Japan.

Salyi, S., Kritikos, M., Åkermark, B. & Sun, L. (2003). *Chem. Eur. J.* **9**, 557–560.

Seyferth, D., Kiwan, A. M. & Sinn, E. (1985). *J. Organomet. Chem.* **281**, 111–118.

Siemens (1994). *SHELXTL*. Version 5.03. Siemens Analytical X-ray Instruments Inc, Madison, Wisconsin, USA.

Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.

Song, L. C., Kadiata, M., Wang, J. T., Wang, R. J. & Wang, H. G. (1988). *J. Organomet. Chem.* **340**, 239–248.

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