metal-organic compounds

A triclinic polymorph of bis(μ_2-ethanethiolato)-1:2κ^2S:S;3:4κ^2S:S-(μ_4-disulfido-1:2:3:4κ^4S:S:S′:S′)tetrakis[tricarbonyliron(II)](2 Fe—Fe)

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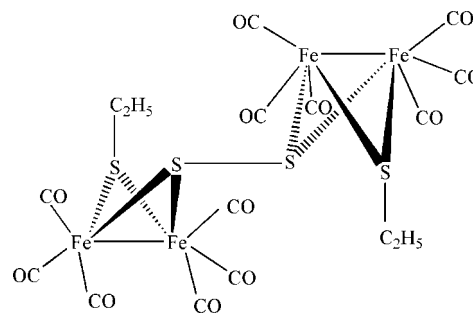Correspondence e-mail: siyoutao@gmail.com

Next to the monoclinic polymorph [Cheng *et al.* (2005). *Acta Cryst.* E**61**, m892–m894], the triclinic title compound, $[Fe_4(C_2H_5S)_2(S_2)(CO)_{12}]$, is the second known form of this composition. The structure is composed of an $[Fe_2(C_2H_5S)(S)(CO)_6]$ subcluster, which is linked to its counterpart by an inversion centre located at the mid-point of the central disulfide bond. The Fe_2S_2 core of each subcluster exhibits a butterfly-like shape, with two S atoms bridging two Fe atoms. In the subcluster, each Fe atom is coordinated in a distorted octahedral coordination by three terminal carbonyl C atoms, two S atoms and one Fe atom. The crystal packing is accomplished through van der Waals interactions.

Related literature

For more details about hydrogenases, including Fe—Fe hydrogenases, see: Darensbourg *et al.* (2000). Two procedures are mainly used for the synthesis of model compounds containing the Fe_2S_2 subcluster of Fe—Fe hydrogenases, see: Lawrence *et al.* (2001); Li & Rauchfuss (2002). The monoclinic polymorph (space group $P2_1/c$) of the title compound has been reported by Cheng *et al.* (2005).

Experimental

Crystal data

$[Fe_4(C_2H_5S)_2(S_2)(CO)_{12}]$	$\gamma = 66.103\,(17)°$
$M_r = 745.88$	$V = 678.2\,(6)$ Å^3
Triclinic, $P\bar{1}$	$Z = 1$
$a = 8.365\,(4)$ Å	Mo $K\alpha$ radiation
$b = 9.296\,(5)$ Å	$\mu = 2.46$ mm^{-1}
$c = 10.209\,(5)$ Å	$T = 293$ K
$\alpha = 87.57\,(2)°$	$0.15 \times 0.12 \times 0.03$ mm
$\beta = 70.082\,(17)°$	

Data collection

Rigaku Mercury70 CCD diffractometer	5323 measured reflections
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)	3060 independent reflections
	1939 reflections with $I > 2\sigma(I)$
$T_{min} = 0.771$, $T_{max} = 1.000$	$R_{int} = 0.036$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	163 parameters
$wR(F^2) = 0.100$	H-atom parameters constrained
$S = 0.99$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
3060 reflections	$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected bond lengths (Å).

Fe1—C1	1.786 (5)	Fe2—C5	1.789 (5)
Fe1—C2	1.793 (5)	Fe2—C6	1.794 (5)
Fe1—C3	1.824 (5)	Fe2—C4	1.806 (5)
Fe1—S1	2.2393 (15)	Fe2—S1	2.2457 (15)
Fe1—S2	2.2688 (16)	Fe2—S2	2.2711 (18)
Fe1—Fe2	2.5183 (15)	S1—S1^i	2.113 (2)

Symmetry code: (i) $-x, -y + 2, -z + 2$.

Data collection: *CrystalClear* (Rigaku, 2002); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *WinGX* (Farrugia, 1999); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2485).

References

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supplementary materials

A triclinic polymorph of bis(μ_2-ethanethiolato)-1:2κ^2S:S;3:4κ^2S:S-(μ_4-disulfido-1:2:3:4κ^4S:S:S':S')tetrakis[tricarbonyliron(II)](2 *Fe-Fe*)

Y. Si, H. Chen and C. N. Chen

Comment

Fe—Fe hydrogenases are enzymes capable of efficiently catalysing the reversible transformation between H^+ and H_2 (Darensbourg *et al.*, 2000). Chemists have been trying to achieve H_2 production technologies of practical use by studying the catalytic process by such kind of hydrogenases, aiming at solving the current energy problem. The well known active site of Fe—Fe hydrogenases, established by X-ray crystallographic and spectroscopic techniques, has an Fe_2S_2 cluster linked to a Fe_4S_4 cuboidal unit by a cysteine-S atom. While the Fe_4S_4 unit is assumed to be reponsible for transferring eletrons, the Fe_2S_2 cluster plays an important role in the catalysis process. Thus, many works concentrate on compounds containing the Fe_2S_2 cluster.

Two kinds of procedures are frequently used to synthesize model substances of the Fe_2S_2 cluster, *e.g.* $Fe_2(SCH_2)_2NR(CO)_6$. The first procedure is a condensation of $(ClCH_2)_2NR$ and $Li_2[Fe_2S_2(CO)_6]$, and the second is a condensation of $Fe_2(SH)_2(CO)_6$ with formaldehyde in the presence of primary amines (Lawrence *et al.*, 2001; Li & Rauchfuss, 2002). In both cases, $LiEt_3BH$ are used to cleave the S—S bond of the starting material $Fe_2S_2(CO)_6$. When trying to get some new complexes using the first procedure, we found some by-products which reflect the diversity of the reactivity of $(FeS)_n$ clusters. Here we report a triclinic polymorph, (I), of $[Fe_4(C_2H_5S)_2(S_2)(CO)_{12}]$. Another monoclinic polymorph (space group $P2_1/c$) has been reported previously (Cheng *et al.*, 2005).

As can be seen in Fig. 1, the crystallographically imposed center of inversion is located at the mid-point of the S1—S1A bond, and thus the asymmetric unit contains one half of the $[Fe_4(C_2H_5S)_2(S_2)(CO)_{12}]$ formula unit. The two Fe atoms of the asymmetric unit (Fe1, Fe2) are linked through an Fe—Fe single bond and are bridged by two S atoms (S1, S2). Thus a butterfly-like arrangement is formed, with a dihedral angle between the two Fe_2S planes being 100.53 (6)°. The average Fe—S bond length is 2.256 (16) Å, and the average Fe—S—Fe angle is 67.9 (6)°. The octahedral coordination geometry around each Fe atom is completed by three carbonyl C atoms [average Fe—C distance 1.799 (14) Å, average C—Fe—C angle 97 (4)°].

The packing diagram is shown in Fig. 2. There is only one molecule in each unit cell, and neighbouring molecules pack along the *a* axis; the crystal is stabilized by van der Waals interactions.

In comparison with the monoclinic polymorph (Cheng *et al.*, 2005), the configuration of the $[Fe_4(C_2H_5S)_2(S_2)(CO)_{12}]$ molecules is different, just like the packing in the crystal.

supplementary materials

Experimental

All experiments were carried out under an atmosphere of purified, oxygen-free and dry nitrogen using standard Schlenk techniques. THF and hexane were dried and freshly distilled prior to use according to standard methods. The commercially available products paraformaldehyde, [Fe(CO)$_5$], LiBEt$_3$H, F$_3$CCOOH and C$_5$H$_9$NH$_2$ were of reagent grade and were used as received. The starting material [Fe$_2$S$_2$(CO)$_6$] was prepared according to the literature.

[Fe$_2$S$_2$(CO)$_6$] (1 mmol, 0.344 g) was dissolved in dry THF (40 ml) under a nitrogen atmosphere and then cooled to 195 K with acetone and liquid nitrogen. After the solution was stirred for 30 minutes, LiBEt$_3$H (2 mmol) was added dropwise very slowly. At the midpoint of the addition, the color of the reaction mixture turned from red to dark green; for the rest of addition it remained green. After another 30 minutes, F$_3$CCOOH (2 mmol, 0.149 ml) was added. The new mixture was stirred for an additional hour. The cool solution was added to a mixture of paraformaldehyde (40 mmol, 1.2 g) and C$_5$H$_9$NH$_2$ (1 mmol, 1.98 ml) in THF which had been stirred for 10 h and cooled to 273 K. The last mixture was stirred for 24 h and the majority of the solvent was evaporated under vacuum. The remaining residual was filtered through silica gel. A red fraction was collected by elution with hexane. Recrystallization of the crude product from fresh distilled pentane in a fridge at 253 K for several days gave the title complex as a by-product in low and varing yields (<5%).

Refinement

Hydrogen atoms were placed at idealized positions and allowed to ride on their parent atoms, with CH$_2$ and CH$_3$ bonds set equal to 0.97 and 0.96 Å, respectively and U_{iso}(H)=1.2U_{eq}(C) for hydrogen atoms of C7, and U$_{iso}$ (H)=1.5U$_{eq}$ (C) for hydrogen atoms of C8. The highest residual peak was located at 0.88 Å from S1.
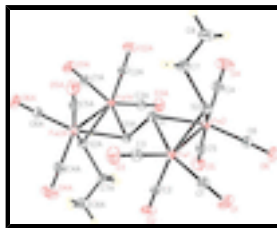
Figures

Fig. 1. The molecular structure of (I), with atom labels and 20% probability displacement ellipsoids for all non-H atoms. [Symmetry operator A: -x, -y + 2, -z + 2.]
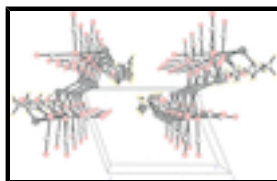

Fig. 2. The packing diagram of (I), viewed down the **b** axis.

bis(μ$_2$-ethanethiolato)-1:2κ^2S:S;3:4κ^2S:S- (μ$_4$-disulfido-1:2:3:4κ^4S:S:S':S')tetrakis [tricarbonyliron(II)](2 *Fe—Fe*)

Crystal data

[Fe$_4$(C$_2$H$_5$S)$_2$(S$_2$)(CO)$_{12}$] Z = 1

$M_r = 745.88$

$F(000) = 370$

Triclinic, $P\overline{1}$

$D_x = 1.826$ Mg m^{-3}

Hall symbol: -P 1

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$a = 8.365$ (4) Å

Cell parameters from 1200 reflections

$b = 9.296$ (5) Å

$\theta = 2.1–27.5°$

$c = 10.209$ (5) Å

$\mu = 2.46$ mm^{-1}

$\alpha = 87.57$ (2)°

$T = 293$ K

$\beta = 70.082$ (17)°

Prism, orange

$\gamma = 66.103$ (17)°

$0.15 \times 0.12 \times 0.03$ mm

$V = 678.2$ (6) Å^3

Data collection

Rigaku Mercury70 CCD diffractometer

3060 independent reflections

Radiation source: fine-focus sealed tube

1939 reflections with $I > 2\sigma(I)$

graphite

$R_{int} = 0.036$

CCD_Profile_fitting scans

$\theta_{max} = 27.5°$, $\theta_{min} = 2.4°$

Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2002)

$h = -10 \rightarrow 10$

$T_{min} = 0.771$, $T_{max} = 1.000$

$k = -11 \rightarrow 11$

5323 measured reflections

$l = -12 \rightarrow 13$

Refinement

Refinement on F^2

Primary atom site location: structure-invariant direct methods

Least-squares matrix: full

Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.048$

Hydrogen site location: inferred from neighbouring sites

$wR(F^2) = 0.100$

H-atom parameters constrained

$S = 0.99$

$w = 1/[\sigma^2(F_o^2) + (0.0419P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

3060 reflections

$(\Delta/\sigma)_{max} < 0.001$

163 parameters

$\Delta\rho_{max} = 0.39$ e Å^{-3}

0 restraints

$\Delta\rho_{min} = -0.42$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

supplementary materials

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	y	z	U_{iso}*/U_{eq}
Fe1	0.31028 (8)	1.00320 (7)	0.78114 (6)	0.03542 (19)
Fe2	0.33627 (9)	0.73745 (7)	0.86174 (7)	0.03887 (19)
S1	0.06448 (15)	0.94806 (12)	0.89480 (11)	0.0364 (3)
S2	0.37128 (16)	0.79317 (13)	0.63756 (12)	0.0425 (3)
O2	0.2904 (5)	1.1642 (4)	1.0304 (4)	0.0659 (10)
O1	0.7064 (5)	0.9407 (5)	0.6498 (4)	0.0765 (12)
O3	0.1430 (6)	1.2810 (4)	0.6441 (4)	0.0801 (13)
O5	0.3256 (6)	0.7693 (4)	1.1491 (4)	0.0767 (12)
C1	0.5507 (7)	0.9675 (5)	0.6996 (5)	0.0485 (12)
O6	0.7439 (5)	0.5643 (5)	0.7670 (5)	0.0864 (14)
C3	0.2065 (7)	1.1746 (6)	0.6958 (5)	0.0477 (12)
C6	0.5855 (8)	0.6296 (6)	0.8033 (5)	0.0559 (14)
C2	0.2944 (6)	1.1039 (5)	0.9341 (5)	0.0444 (11)
C5	0.3261 (7)	0.7589 (5)	1.0381 (6)	0.0527 (13)
C4	0.2657 (8)	0.5763 (6)	0.8735 (6)	0.0601 (14)
O4	0.2224 (8)	0.4741 (5)	0.8805 (6)	0.1078 (17)
C7	0.1744 (7)	0.8070 (6)	0.5873 (5)	0.0546 (13)
H7A	0.0604	0.8465	0.6691	0.065*
H7B	0.1589	0.8820	0.5186	0.065*
C8	0.2037 (11)	0.6549 (7)	0.5290 (9)	0.124 (3)
H8A	0.0984	0.6666	0.5044	0.187*
H8B	0.2173	0.5809	0.5972	0.187*
H8C	0.3149	0.6166	0.4468	0.187*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0322 (4)	0.0369 (4)	0.0375 (4)	−0.0163 (3)	−0.0103 (3)	0.0028 (3)
Fe2	0.0377 (4)	0.0317 (3)	0.0461 (4)	−0.0122 (3)	−0.0159 (3)	0.0021 (3)
S1	0.0297 (6)	0.0386 (6)	0.0380 (6)	−0.0142 (5)	−0.0079 (5)	−0.0008 (5)
S2	0.0354 (6)	0.0472 (7)	0.0405 (6)	−0.0142 (5)	−0.0110 (5)	−0.0050 (5)
O2	0.078 (3)	0.079 (2)	0.058 (2)	−0.048 (2)	−0.024 (2)	−0.0046 (19)
O1	0.044 (2)	0.109 (3)	0.076 (3)	−0.041 (2)	−0.008 (2)	0.001 (2)
O3	0.086 (3)	0.063 (2)	0.086 (3)	−0.018 (2)	−0.042 (3)	0.027 (2)
O5	0.092 (3)	0.077 (3)	0.057 (2)	−0.020 (2)	−0.040 (2)	0.009 (2)
C1	0.045 (3)	0.055 (3)	0.046 (3)	−0.025 (3)	−0.011 (2)	0.005 (2)
O6	0.045 (2)	0.079 (3)	0.110 (3)	0.004 (2)	−0.029 (2)	−0.025 (2)
C3	0.052 (3)	0.048 (3)	0.045 (3)	−0.022 (2)	−0.019 (2)	0.008 (2)
C6	0.049 (3)	0.049 (3)	0.066 (4)	−0.010 (3)	−0.026 (3)	−0.005 (3)
C2	0.037 (3)	0.049 (3)	0.053 (3)	−0.024 (2)	−0.015 (2)	0.007 (2)
C5	0.053 (3)	0.043 (3)	0.056 (3)	−0.010 (2)	−0.023 (3)	0.008 (2)
C4	0.075 (4)	0.047 (3)	0.071 (4)	−0.030 (3)	−0.036 (3)	0.015 (3)
O4	0.150 (5)	0.074 (3)	0.149 (4)	−0.078 (3)	−0.076 (4)	0.033 (3)
C7	0.050 (3)	0.062 (3)	0.058 (3)	−0.021 (3)	−0.027 (3)	−0.001 (3)

C8	0.131 (7)	0.086 (5)	0.194 (9)	−0.029 (5)	−0.116 (7)	−0.027 (5)

Geometric parameters (Å, °)

Fe1—C1	1.786 (5)	O2—C2	1.137 (5)
Fe1—C2	1.793 (5)	O1—C1	1.145 (5)
Fe1—C3	1.824 (5)	O3—C3	1.123 (5)
Fe1—S1	2.2393 (15)	O5—C5	1.140 (6)
Fe1—S2	2.2688 (16)	O6—C6	1.138 (6)
Fe1—Fe2	2.5183 (15)	C4—O4	1.138 (6)
Fe2—C5	1.789 (5)	C7—C8	1.451 (7)
Fe2—C6	1.794 (5)	C7—H7A	0.9700
Fe2—C4	1.806 (5)	C7—H7B	0.9700
Fe2—S1	2.2457 (15)	C8—H8A	0.9600
Fe2—S2	2.2711 (18)	C8—H8B	0.9600
S1—S1ⁱ	2.113 (2)	C8—H8C	0.9600
S2—C7	1.842 (5)		
C1—Fe1—C2	90.8 (2)	C4—Fe2—Fe1	149.28 (16)
C1—Fe1—C3	99.4 (2)	S1—Fe2—Fe1	55.72 (4)
C2—Fe1—C3	99.1 (2)	S2—Fe2—Fe1	56.27 (4)
C1—Fe1—S1	157.40 (15)	S1ⁱ—S1—Fe1	111.12 (8)
C2—Fe1—S1	94.02 (15)	S1ⁱ—S1—Fe2	111.36 (8)
C3—Fe1—S1	101.64 (16)	Fe1—S1—Fe2	68.32 (5)
C1—Fe1—S2	87.52 (16)	C7—S2—Fe1	114.87 (16)
C2—Fe1—S2	156.70 (15)	C7—S2—Fe2	113.05 (18)
C3—Fe1—S2	104.06 (16)	Fe1—S2—Fe2	67.38 (5)
S1—Fe1—S2	79.39 (5)	O1—C1—Fe1	177.8 (5)
C1—Fe1—Fe2	101.44 (15)	O3—C3—Fe1	179.3 (5)
C2—Fe1—Fe2	101.42 (15)	O6—C6—Fe2	178.4 (5)
C3—Fe1—Fe2	150.37 (16)	O2—C2—Fe1	177.7 (4)
S1—Fe1—Fe2	55.96 (4)	O5—C5—Fe2	177.8 (5)
S2—Fe1—Fe2	56.35 (5)	O4—C4—Fe2	179.6 (6)
C5—Fe2—C6	90.6 (2)	C8—C7—S2	111.8 (4)
C5—Fe2—C4	99.0 (2)	C8—C7—H7A	109.3
C6—Fe2—C4	100.4 (2)	S2—C7—H7A	109.3
C5—Fe2—S1	94.44 (15)	C8—C7—H7B	109.3
C6—Fe2—S1	156.35 (18)	S2—C7—H7B	109.3
C4—Fe2—S1	101.55 (18)	H7A—C7—H7B	107.9
C5—Fe2—S2	158.11 (17)	C7—C8—H8A	109.5
C6—Fe2—S2	87.54 (17)	C7—C8—H8B	109.5
C4—Fe2—S2	102.75 (18)	H8A—C8—H8B	109.5
S1—Fe2—S2	79.21 (5)	C7—C8—H8C	109.5
C5—Fe2—Fe1	102.83 (16)	H8A—C8—H8C	109.5
C6—Fe2—Fe1	100.63 (17)	H8B—C8—H8C	109.5

Symmetry codes: (i) −x, −y+2, −z+2.

Fig. 1

Fig. 2