

Bis(μ_4 -butane-1,4-dithiolato)bis[hexa-carbonyldiiron(II)(Fe—Fe)]

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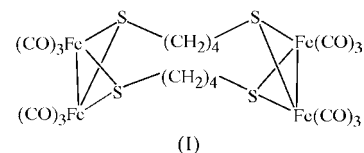
The novel title double-butterfly Fe/S cluster complex, $[\text{Fe}_4(\text{C}_4\text{H}_8\text{S}_2)_2(\text{CO})_{12}]$, which is structurally similar to the active site of the Fe-only hydrogenases, contains two inversion-related $\text{Fe}_2\text{S}_2(\text{CO})_6$ subcluster cores connected by two equivalent butyl chains to afford a 16-membered macrocycle. The formation of the 16-membered macrocycle has an influence on the C—S—Fe angles, while the Fe—Fe and Fe—S bond lengths remain similar to those in related complexes.

Comment

Recently, with the shortage of fossil fuels, hydrogen, as a kind of much needed and clean energy, has attracted growing attention. Unfortunately, its high cost has become a bottleneck that has limited its wide application. Consequently, scientists have been looking for a new route to prepare hydrogen, and the Fe-only hydrogenases, as effective enzymes for the production of molecular hydrogen in biological systems, have become of particular interest (Georgakaki *et al.*, 2003; Artero & Fontecave, 2005). With advances in X-ray crystallographic and spectroscopic techniques for macromolecules, detailed structures of the Fe-only hydrogenases have been determined (Peters *et al.*, 1998; Nicolet *et al.*, 1999). The active site is composed of an Fe_2S_2 core bound to a cuboidal Fe_4S_4 cluster *via* the cysteine S atom. To enhance the efficiency and activity of the Fe-only hydrogenases, scientists have designed and simulated many kinds of models of the active site (Gao *et al.*, 2007; Song *et al.*, 2006; Schwartz *et al.*, 2006). On the basis of our previous work on the Fe_2S_2 core of the Fe-only hydrogenases (Hu *et al.*, 2006, 2007; Cheng *et al.*, 2005; Si *et al.*, 2007), we have successfully prepared a new double-butterfly Fe/S cluster complex containing a 16-membered macrocycle formed by the linking of two $\text{Fe}_2\text{S}_2(\text{CO})_6$ subcluster cores through two butyl chains.

The title compound, (I), is a centrosymmetric double-butterfly cluster complex with two identical butterfly $\text{Fe}_2\text{S}_2(\text{CO})_6$ subcluster cores linked together through two

identical butyl chains (Fig. 1). The resulting 16-membered macrocycle thus includes four Fe atoms, four S atoms and eight C atoms. This kind of macrocyclic complex is relatively rare; reported examples include $[\{\text{Fe}_2(\text{CO})_5(\mu\text{-SCH}_2)_2\text{NCH}_2\text{-CH}_2\text{N}(\mu\text{-SCH}_2)_2\text{Fe}_2(\text{CO})_5\}(\text{Ph}_2\text{PCH}_2)_2]$, (II) (Gao *et al.*, 2006), with a 14-membered macrocycle, $[\text{Fe}_2(\text{CO})_6]_2[\mu\text{-SCH}_2(\text{CH}_2\text{OCH}_2)_2\text{CH}_2\text{S-}\mu]_2$, (III) (Song *et al.*, 2004), with a 24-membered macrocycle, and $[\text{Fe}_2(\text{CO})_6]_2[\mu\text{-SCH}_2(\text{CH}_2\text{OCH}_2)_3\text{CH}_2\text{S-}\mu]_2$, (IV) (Song *et al.*, 2004), with a 30-membered macrocycle. Complex (II) is different from (I) and the other complexes in that the bridges between the iron fragments are different so the complex is not symmetrical. Although (III) and (IV) are very similar to (I) structurally, they form macrocycles through long ether chains $[-\text{CH}_2(\text{CH}_2\text{OCH}_2)_n\text{-CH}_2-]$, with $n = 2$ and 3, respectively], while (I) provides a new synthetic route to form such a macrocycle through alkyl chains.



The formation of the macrocycle has a slight lengthening influence on the Fe1—Fe2 distance (Table 1) compared to the corresponding distances in $[\{(\mu\text{-pdt})\text{Fe}_2\}(\text{CO})_6]$, (V) [2.5103 (11) Å; pdt is propane-1,3-dithiolate; Lyon *et al.*, 1999], and (III) [2.5130 (14) Å], while lying between the Fe1—Fe2 [2.5197 (8) Å] and Fe3—Fe4 [2.5387 (8) Å] distances in (II). The average Fe—S bond length in (I) [2.2599 (12) Å] is slightly longer than that in (V) [2.2516 (10) Å]. The C—S—Fe angles in (I) show small variations (Table 2) compared to those of $[\{(\text{Et}_2\text{NC}=\text{CNET}_2)\text{Fe}_2\text{S}_2\}(\text{CO})_6]$ [C1—S1—Fe1 = 104.0 (2)°, C1—S2—Fe1 = 102.02 (19)°, C2—S2—Fe1 = 103.70 (19)° and C2—S2—Fe2 = 102.73 (19)°; Siebenlist *et al.*, 2002]. Compared with S1—Fe—S2 in (V) [85.27 (4)°], the S—Fe—S angles of (I) [S2—Fe1—S1 = 80.37 (4)° and S2—Fe2—S1 = 80.30 (5)°] are smaller because of the different size of the macrocycle. In addition, the C7—S2...S1 angle is 160.0°.

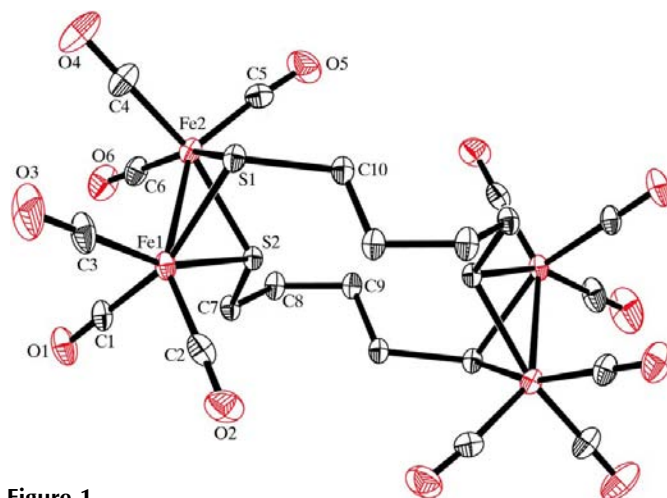


Figure 1
The molecular structure of (I), shown with 20% probability displacement ellipsoids.

which shows that the C7—S2 bond is approximately equatorial with respect to the line connecting the wingtip atoms S1 and S2, while C10—S1···S2 is 100.1°, which shows that the C10—S1 bond is axial with respect to the span between the wingtip S atoms. In contrast, both C—S···S angles in [Fe₂(SPh-2-OMe)₂(CO)₆] are *ca* 160°, which indicates that both the C—S bonds are equatorial with respect to the S···S line across the wingtips (Si *et al.*, 2005).

Experimental

All reactions were carried out under dry oxygen-free N₂ using standard Schlenk techniques. Tetrahydrofuran (THF) and *n*-hexane were dried and distilled prior to use according to standard methods. Commercially available butane-1,4-dithiol and Fe₃(CO)₁₂ were of reagent grade and were used as received. Fe₃(CO)₁₂ (3 mmol, 1.5 g) was dissolved in dry THF (50 ml) under an N₂ atmosphere and butane-1,4-dithiol (3 mmol, 0.353 ml) was added. The solution was stirred at 343 K for 90 min and the color changed from dark green to dark red. After cooling to room temperature, the majority of the solvent was evaporated under vacuum, and the remaining solution was purified through silica gel. A red fraction was collected and (I) was obtained as dark-red crystals from hexane (yield 7%). Elemental analysis calculated for C₂₀H₁₆Fe₄O₁₂S₄: C 30.03, H 2.02%; found: C 30.97, H 2.15%. IR (KBr pellet, cm⁻¹): ν_{CO} 2070 (*m*), 2030 (*s*), 1984 (*vs*). *m/z*: 823.1 (*M* + Na⁺).

Crystal data

[Fe ₄ (C ₄ H ₈ S ₂) ₂ (CO) ₁₂]	γ = 69.718 (16)°
<i>M_r</i> = 799.97	<i>V</i> = 750.0 (7) Å ³
Triclinic, <i>P</i> 1̄	<i>Z</i> = 1
<i>a</i> = 7.765 (4) Å	Mo Kα radiation
<i>b</i> = 9.712 (5) Å	μ = 2.23 mm ⁻¹
<i>c</i> = 11.036 (6) Å	<i>T</i> = 295 K
α = 82.445 (17)°	0.5 × 0.3 × 0.15 mm
β = 74.035 (17)°	

Data collection

Mercury CCD diffractometer	5772 measured reflections
Absorption correction: empirical (using intensity measurements) (SADABS; Sheldrick, 1996)	3378 independent reflections
<i>T</i> _{min} = 0.46, <i>T</i> _{max} = 0.72	2413 reflections with <i>I</i> > 2σ(<i>I</i>)
	<i>R</i> _{int} = 0.020

Refinement

<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.037	181 parameters
<i>wR</i> (<i>F</i> ²) = 0.106	H-atom parameters constrained
<i>S</i> = 1.00	Δρ _{max} = 0.56 e Å ⁻³
3378 reflections	Δρ _{min} = -0.46 e Å ⁻³

H atoms were placed at idealized positions [C—H = 0.97 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C)] and treated as riding atoms.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

Table 1

Selected geometric parameters (Å, °).

Fe1—C1	1.784 (4)	Fe2—C4	1.786 (4)
Fe1—C3	1.798 (4)	Fe2—C6	1.791 (4)
Fe1—C2	1.808 (4)	Fe2—C5	1.798 (4)
Fe1—S2	2.2460 (12)	Fe2—S2	2.2528 (12)
Fe1—S1	2.2721 (12)	Fe2—S1	2.2687 (13)
Fe1—Fe2	2.5263 (14)		
C7—S2—Fe1	115.19 (10)	C10—S1—Fe2	111.11 (11)
C7—S2—Fe2	114.89 (12)	C10—S1—Fe1	115.56 (12)

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3090). Services for accessing these data are described at the back of the journal.

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