

Mixed-chalcogenide double-butterfly complex $[\{(CO)_6Fe_2SSe\}_2-\mu-C(H)-C(H)]$

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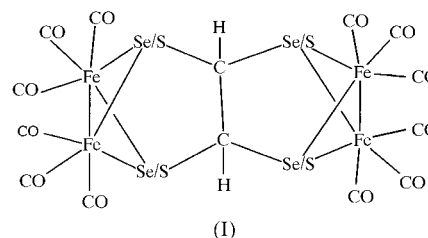
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Bubbling acetylene gas slowly through a methanol solution of $[(CO)_6Fe_2\{\mu-SSe\}]$ containing sodium acetate for 48 h at room temperature yields the double-butterfly complex μ -[ethane-1,1,2,2-tetra(selenido/sulfido)]bis[hexacarbonyldiiron($Fe-Fe$)], $[Fe_4(C_2H_2S_2Se_2)(CO)_{12}]$. The molecular structure was established by single-crystal X-ray diffraction techniques. The structure consists of two Fe_2SSe butterfly units linked to each other through a bridging HC—CH group. The molecule has twofold symmetry and the two Fe atoms have distorted octahedral geometries.

Comment

Bonding and reactivity studies of alkynes attached to metal centres are of considerable interest because of the potential of the coordinated alkynes to be transformed into useful organic species (Katz & Hacker, 1985). In contrast to the large number of reports on the different bonding modes between alkynes and transition metals (Sappa *et al.*, 1983), studies of complexes in which alkynes are attached to main group elements are more recent and relatively few (Mathur, 1997). Recent successes in the area of incorporating group 16 elements into transition metal carbonyl complexes have evoked interest in studying the interaction of alkynes with these ligands. The facile addition of phenylacetylene to $(CO)_6Fe_2(\mu-Se_2)$ and $(CO)_6Fe_2(\mu-EE')$ occurs at room temperature to form $(CO)_6Fe_2\{\mu-SeC(H)=C(Ph)Se\}$ and $(CO)_6Fe_2\{\mu-EC(H)=C(Ph)E'\}$, respectively, whereas $(CO)_6Fe_2(\mu-S_2)$ and $(CO)_6Fe_2(\mu-Te_2)$ are inert towards such addition under similar reaction conditions (Mathur, Hossain *et al.*, 1995). In $(CO)_6Fe_2\{\mu-SeC(H)=C(Ph)Se\}$, the reactive Se sites are blocked, and addition of $Pt(PPh_3)_2$ (Mathur, Hossain, Das & Sinha, 1993) and $(CO)_6Fe_2(\mu-Se_2)$ (Mathur & Hossain, 1993) occurs readily across the C=C bond to yield products in which the

acetylenic bond is reduced. Similarly, addition of organometallic groups across the Fe—Fe bond can be carried out thermolytically, as in the formation of Se-bridged mixed-metal clusters $Cp_2Mo_2Fe_2(CO)_6(\mu_4-Se)(\mu_3-Se)_2$ (Mathur, Hossain & Rheingold, 1993). We report here the structural characterization of a mixed-chalcogenide double-butterfly complex, (I), obtained from the reaction of $(CO)_6Fe_2(\mu-SSe)$ with acetylene. The starting material provides an important probe to the active metallic centre in enzymatic processes (Pombeiro & Richards, 1990).



In the structure of (I), the Se and S positions are disordered with equal occupancy (50%). The molecule contains a twofold axis bisecting the C7—C7' bond. The structure can be described as two Fe_2SSe core units linked to each other through a bridging HC—CH group. As a result of the acetylene addition to the Fe_2SSe tetrahedron, the acetylenic bond is reduced to beyond an olefinic bond order. The C7—C7' bond distance of 1.511 (16) Å in $[\{(CO)_6Fe_2SSe\}_2\{\mu-C(H)C(H)\}]$ is similar to that observed in $[\{(CO)_6Fe_2SSe\}_2\{\mu-C(H)C(Ph)\}]$ [1.53(1) Å; Mathur, Dash *et al.*, 1996], whereas it is longer than the corresponding bond lengths of 1.48 (1) Å in $[\{(CO)_6Fe_2Se_2\}_2\{\mu-C(H)C(Ph)\}]$ (Mathur & Hossain, 1993), 1.47 (1) Å in $(CO)_6Fe_2\{\mu-Te(CH_2)_2Te\}$ (Shieh & Shieh, 1994), 1.494 Å in $(CO)_6Fe_2\{\mu-Se(CH_2)_2Se\}$ (Mathur, Manimaran *et al.*, 1996) and 1.42 (1) Å in $[(CO)_6Fe_2\{\mu-SeC(H)C(Ph)\}-Pt(PPh_3)_2]$ (Mathur, Hossain & Rheingold, 1993). Each Fe atom has three CO groups bonded to it. The μ_3-S ligand, the μ_3-Se ligand and the Fe—Fe bond define a distorted octahedral geometry around each Fe centre.

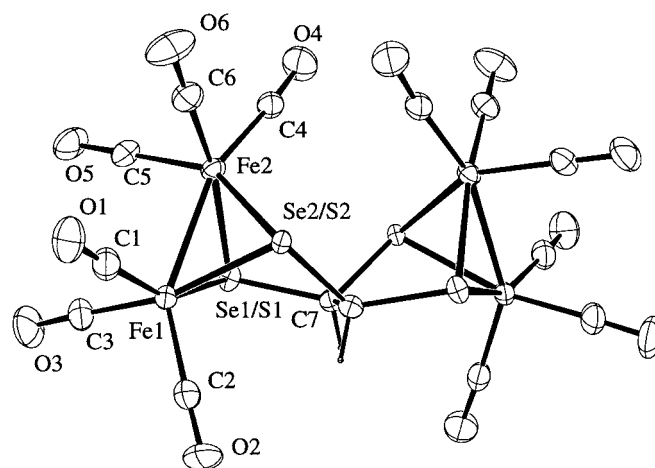


Figure 1
The structure of the title compound showing 30% probability displacement ellipsoids.

Experimental

In a typical procedure, acetylene gas was bubbled at a slow rate with constant stirring into a methanol solution (15 ml) containing freshly prepared $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ (0.6 g, 1.53 mmol) (Mathur, Sekar *et al.*, 1995) and anhydrous sodium acetate (0.25 g). The reaction was monitored by thin-layer chromatography (TLC) and terminated after 48 h at room temperature when all the $(\text{CO})_6\text{Fe}_2(\mu\text{-SSe})$ had been consumed. Chromatographic work-up on silica-gel TLC plates using a 2:3 solution mixture of CH_2Cl_2 –hexane yielded an orange band of $[\{(\text{CO})_6\text{Fe}_2\text{SSe}_2\{\mu\text{-C(H)C(H)}\}]$ in 28% yield. Rectangular-shaped air-stable crystals of $[\{(\text{CO})_6\text{Fe}_2\text{SSe}_2\{\mu\text{-C(H)C(H)}\}]$ were obtained by slow evaporation from a mixture of CH_2Cl_2 –hexane solution at 263 K. IR data (ν , CH_2Cl_2): 2080 (s), 2068 (s), 2042 (s), 2009 (s), 1997 (m) cm^{-1} .

Crystal data

$[\text{Fe}_4(\text{C}_2\text{H}_2\text{S}_2\text{Se}_2)(\text{CO})_{12}]$
 $M_r = 807.60$
 Orthorhombic, *Fdd2*
 $a = 6.531(2) \text{ \AA}$
 $b = 44.759(4) \text{ \AA}$
 $c = 16.224(2) \text{ \AA}$
 $V = 4742.6(16) \text{ \AA}^3$
 $Z = 8$
 $D_x = 2.262 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 8.02\text{--}12.21^\circ$
 $\mu = 5.701 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Rectangular, orange
 $0.375 \times 0.134 \times 0.126 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.323$, $T_{\max} = 0.488$
 6094 measured reflections
 2449 independent reflections
 2188 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$
 $\theta_{\text{max}} = 27.44^\circ$
 $h = -8 \rightarrow 0$
 $k = -18 \rightarrow 58$
 $l = -19 \rightarrow 21$
 3 standard reflections
 frequency: 60 min
 intensity decay: 2%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.108$
 $S = 1.095$
 2449 reflections
 154 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0473P)^2 + 78.9306P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.48 \text{ e \AA}^{-3}$

The data were originally collected in the monoclinic system and the structure solved in space group *Cc*. Additional symmetry was observed and the structure was found to transform to the orthorhombic system (space group *Fdd2*). The Se and S positions were found to be disordered, so their occupancies were fixed at 50% and they were constrained to have the same positional coordinates and the same anisotropic displacement parameters. The H atom was fixed geometrically and not refined. During refinement, the structure was treated as a racemic twin. The occupancy of the major component refined to a value of 0.515.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *NRCVAX*; software used to prepare material for publication: *SHELXL97*.

Table 1

Selected geometric parameters (\AA , $^\circ$).

Se1/S1–C7	1.916 (7)	Se2/S2–Fe1	2.343 (1)
Se1/S1–Fe1	2.334 (2)	Se2/S2–Fe2	2.364 (1)
Se1/S1–Fe2	2.346 (2)	Fe1–Fe2	2.514 (2)
Se2/S2–C7 ⁱ	1.931 (8)		
C7–Se1/S1–Fe1	103.2 (2)	C1–Fe1–Fe2	96.4 (3)
C7–Se1/S1–Fe2	99.5 (2)	Se1/S1–Fe1–Fe2	57.8 (1)
Fe1–Se1/S1–Fe2	65.0 (1)	Se2/S2–Fe1–Fe2	58.1 (1)
C7 ⁱ –Se2/S2–Fe1	96.1 (2)	C5–Fe2–C6	91.0 (4)
C7 ⁱ –Se2/S2–Fe2	106.4 (2)	C5–Fe2–C4	98.5 (4)
Fe1–Se2/S2–Fe2	64.5 (1)	C6–Fe2–C4	93.0 (4)
C2–Fe1–C3	99.0 (5)	C5–Fe2–Se1/S1	90.0 (3)
C2–Fe1–C1	100.4 (5)	C6–Fe2–Se1/S1	164.2 (3)
C3–Fe1–C1	91.2 (5)	C4–Fe2–Se1/S1	102.4 (3)
C2–Fe1–Se1/S1	106.4 (4)	C5–Fe2–Se2/S2	146.2 (3)
C3–Fe1–Se1/S1	88.9 (3)	C6–Fe2–Se2/S2	88.7 (3)
C1–Fe1–Se1/S1	152.9 (3)	C4–Fe2–Se2/S2	115.2 (3)
C2–Fe1–Se2/S2	96.0 (3)	Se1/S1–Fe2–Se2/S2	81.8 (1)
C3–Fe1–Se2/S2	164.4 (3)	C5–Fe2–Fe1	90.8 (3)
C1–Fe1–Se2/S2	90.5 (3)	C6–Fe2–Fe1	107.0 (3)
Se1/S1–Fe1–Se2/S2	82.6 (1)	C4–Fe2–Fe1	157.8 (3)
C2–Fe1–Fe2	149.3 (3)	Se1/S1–Fe2–Fe1	57.3 (1)
C3–Fe1–Fe2	106.2 (3)	Se2/S2–Fe2–Fe1	57.3 (1)

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, z$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1109). Services for accessing these data are described at the back of the journal.

References

- Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Katz, T. J. & Hacker, S. M. (1985). *J. Am. Chem. Soc.* **107**, 2182–2183.
- Mathur, P. (1997). *Adv. Organomet. Chem.* **41**, 243–314.
- Mathur, P., Dash, A. K., Hossain, M. M., Chen, Y.-S., Holt, E. M. & Rao, S. N. (1996). *J. Organomet. Chem.* **526**, 379–383.
- Mathur, P. & Hossain, M. M. (1993). *Organometallics*, **12**, 2398–2400.
- Mathur, P., Hossain, M. M., Das, K. & Sinha, U. C. (1993). *J. Chem. Soc. Chem. Commun.* pp. 46–48.
- Mathur, P., Hossain, M. M. & Rheingold, A. L. (1993). *Organometallics*, **12**, 5029–5031.
- Mathur, P., Hossain, M. M., Umbarkar, S. B., Satyanarayana, C. V. V., Tavale, S. S. & Puranik, V. G. (1995). *Organometallics*, **14**, 959–963.
- Mathur, P., Manimaran, B., Trivedi, R., Hossain, M. M. & Arabati, M. (1996). *J. Organomet. Chem.* **515**, 155–162.
- Mathur, P., Sekar, P., Satyanarayana, C. V. V. & Mahon, M. F. (1995). *Organometallics*, **14**, 2115–2118.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Pombeiro, A. J. L. & Richards, R. L. (1990). *Coord. Chem. Rev.* **104**, 13–38.
- Sappa, E., Tiripicchio, A. & Braunstein, P. (1983). *Chem. Rev.* **83**, 203–239.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. Release 97–1. University of Göttingen, Germany.
- Shieh, M. & Shieh, M.-H. (1994). *Organometallics*, **13**, 920–924.