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Two silicon-bridged cyclopentadienyl Fe_2S_4 cluster units connected through an $Fe(III)S_6$ unit. Crystal and molecular structure of $[((CH_3)_2SiCp'_2)_2Fe_5(\mu_3\text{-}S_2)_2(\mu_4\text{-}S_2)_2(\mu_4\text{-}S_4)]FeCl_4$

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Abstract

The reaction of $(CH_3)_2Si[Cp'Fe(CO)_2]_2$ with elemental sulfur in refluxing toluene resulted in the formation of two new iron–sulfur cluster compounds. Prolonged crystallisation from CH_2Cl_2–hexane mixtures of one of these compounds resulted in crystals of the title compound. An X-ray diffraction study revealed that two $(CH_3)_2SiCp'_2Fe_2$ units are connected to a central Fe(III) ion via four disulfido ligands and a tetrasulfido ligand. This iron atom is octahedrally coordinated by six sulfur atoms. Of the six Fe(III)–S distances four are close to 2.30 Å and the other two are about 2.20 Å. In both the $(CH_3)_2SiCp'_2Fe_2$ units each iron atom is coordinated to three sulfur atoms and one Cp ring. This results in twelve Fe–S distances six of them are in a narrow range from 2.165 to 2.184 Å, whereas the other six vary from 2.240 to 2.286 Å. The Fe–Fe distances are 2.561 and 2.581 Å. The S–S distances range from 2.041 to 2.073 Å. The Fe–Cl distances in the $FeCl_4^-$ ion, centred around 2.16 Å, show the presence of Fe(III) in this ion.

Key words: Crystal structures; Iron complexes; Silicon complexes; Cyclopentadienyl complexes; Cluster complexes

The rigid strain imposed by XCp'_2 bridged ligands ($X = SiMe_2$, CH_2; $Cp' = C_5H_4$) in dinuclear complexes has a striking influence on the structure and properties of these compounds as compared to their non-bridged counterparts, most often ascribed to the close proximity of the two metal centres [1].

To obtain a better insight into the cooperative effects of two neighbouring metal centres we prepared some iron sulfur cyclopentadienyl cluster compounds in which the Cp′ ligands are bridged by a silicon atom, i.e. with $Me_2SiCp'_2$ as the ligand.

A wealth of di- and tetranuclear iron sulfur cluster compounds has been synthesised from the reaction of the dimeric $[Fe(CO)_2Cp]_2$ compounds ($Cp = C_5H_5$, C_5H_4Me or C_5Me_5) with elemental sulfur [2–7]. Following this procedure, the analogous reaction between $(CH_3)_2Si[Cp'Fe(CO)_2]_2$[†, ††] [8, 9] and sulfur (Fe:S atomic ratio 1:6) in refluxing toluene for 72 h resulted in the formation of two new cluster compounds **2** and **3** (eqn. (1)). **2** and **3** were isolated separately as black powders, due to their different solubility in toluene.

$$\underset{\mathbf{1}}{(CH_3)_2Si[Cp'Fe(CO)_2]_2} + S_8 \longrightarrow \underset{\mathbf{2}}{[(CH_3)_2SiCp'_2)_2Fe_4(\mu_3\text{-}S)_2(\mu_3\text{-}S_2)_2]} + \mathbf{3} \qquad (1)$$

2 belongs to the class of Fe_4S_6 cluster compounds, and compared to other clusters of this class [6, 10], it shows a remarkable thermal stability. Full details of the isolation and characterisation of this cluster will be published elsewhere [11].

Prolonged attempts (8 weeks) to crystallise **3** from CH_2Cl_2–hexane mixtures under nitrogen revealed the simultaneous occurrence of decomposition and redox processes. **3** appeared to be reactive towards freshly distilled dichloromethane as was recently found for other iron sulfur clusters [10].

$$\underset{\mathbf{4^+}}{[((CH_3)_2SiCp'_2)_2Fe_5(\mu_3\text{-}S_2)_2(\mu_4\text{-}S_2)_2(\mu_4\text{-}S_4)]^+}$$

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[†] Differing from the method by which **1** was first synthesised [8] we prepared **1** by a photochemical reaction of 6 h from $Fe(CO)_5$ (30 mmol) with $(CH_3)_2Si(Cp'H)$ (12 mmol) dissolved in diethyl ether (400 ml). As a light source a Hg high pressure lamp was used. The product was isolated by column chromatography on silica using hexane/toluene (1/1) as the eluent (yield 32%).

[††] Bridged biscp ligands have rarely been used in transition metal(poly)sulfur cluster chemistry, see ref. 9.

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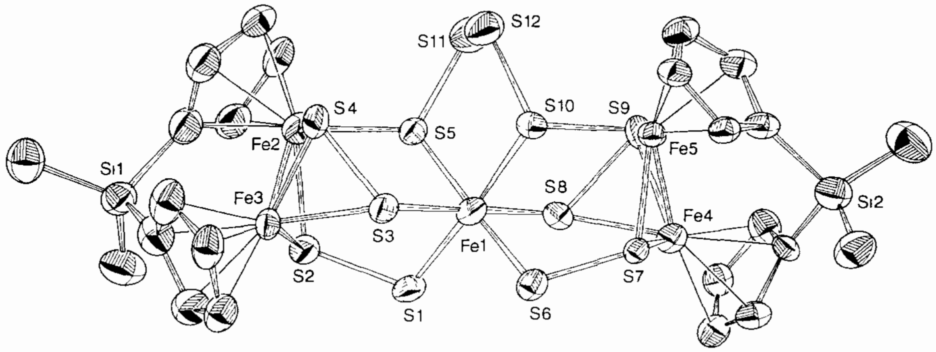

Fig 1. ORTEP [13] drawing of $\mathbf{4}^+$. Thermal ellipsoids are at 50% probability. Hydrogen atoms omitted for clarity. Selected bond distances are: Fe2–Fe3 2.561(2), Fe4–Fe5 2.581(2), Fe1–S1 2.215(2), Fe1–S3 2.305(3), Fe1–S5 2.300(2), Fe1–S6 2.186(2), Fe1–S8 2.299(3), Fe1–S10 2.321(2), Fe2–S2 2.251(2), Fe2–S4 2.181(3), Fe2–S5 2.240(2), Fe3–S2 2.165(3), Fe3–S3 2.286(3), Fe3–S4 2.175(3), Fe4–S7, 2.169(3), Fe4–S8 2.274(2), Fe4–S9 2.180(2), Fe5–S7 2.241(2), Fe5–S9 2.184(3), Fe5–S10 2.256(3), S1–S2 2.067(3), S3–S4 2.068(3), S5–S11 2.058(3), S6–S7 2.067(3), S8–S9 2.068(3), S10–S12 2.073(3), S11–S12 2.041(4), Fe6–Cl1 2.162(5), Fe6–Cl2 2.170(4), Fe6–Cl3 2.155(6), Fe6–Cl4 2.167(6).

These attempts ultimately resulted in a crystal with composition $\mathbf{4}^+FeCl_4^- \cdot 0.5CH_2Cl_2$, suitable for an X-ray diffraction study*.

The molecular structure of $\mathbf{4}^+$ is displayed in Fig. 1. The ion has a bow-tie shaped form and is built up from two $(CH_3)_2SiCp'_2Fe_2$ units. Both units are coordinated by four disulfido ligands and a tetrasulfido ligand to a central Fe(III) ion. This central iron atom is in this way octahedrally coordinated by six sulfur atoms. Four of the six Fe–S distances are close to 2.30 Å, whereas the two other Fe–S distances, involving the two-coordinated sulfur atom of a μ_3-S_2 ligand are about 2.20 Å. The Fe–S distances of about 2.30 Å are similar to those found in the $Fe(SR)_6$ bridge subunit of the $Mo_2Fe_7S_8(SR)_{12}^{3-}$ cluster [14] and they are close to the Fe–S distances found in many other Fe(III) coordination complexes with ligating sulfur atoms, e.g. for $Fe(R_2dtc)_3$ values of 2.34 Å are reported [15].

In both the $(CH_3)_2SiCp'_2Fe_2$ units each iron atom is coordinated to three sulfur atoms and one Cp ring. This results in twelve Fe–S distances, which fall into two categories. Six of them are in a narrow range from 2.165 to 2.184 Å, whereas the other six are somewhat larger, but also in a narrow range, i.e. 2.240–2.286 Å. The Fe–Fe distances are relatively short, 2.561 and 2.581 Å. The S–S distances in all the sulfido ligands were found in the remarkably narrow range of 2.041 to 2.073 Å, and these values are close to those found in H_2S_2, 2.055 Å [10, 16].

The Fe–Cl distances in the $FeCl_4^-$ ion, centred around 2.16 Å, show unambiguously the presence of Fe(III) in this ion [17] and thus gave evidence for the plus one charge on $\mathbf{4}^+$. Whether or not reduced $\mathbf{4}^+$ (i.e. **4**) and **3** are identical cluster compounds is presently being investigated.

Supplementary material

The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK.

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*A crystal of dimensions 0.59×0.26×0.13 mm was mounted in a glass capillary. X-ray data were collected on an Enraf-Nonius CAD4 diffractometer. For experimental details see ref. 12a. A total of 14579 unique reflections was measured of which 6131 were observed. The structure was determined using PATTY and DIRDIF [12b] and final refinement was done using SHELX-76 [12c], up to $R = 0.064$ ($R_w = 0.079$) The dichloromethane molecule appeared to be disordered and could be refined with 0.5 occupancy. Crystal data: $C_{24}H_{28}Cl_4Fe_6S_{12}Si_2 \cdot 0.5CH_2Cl_2$, $M_r = 1277.7$, $T = 293$, triclinic, space group $P\bar{1}$ (*No.* 2), $a = 8.5758(7)$, $b = 15.1606(8)$, $c = 16.5034(7)$ Å, $\alpha = 92.66(1)$, $\beta = 90.50(1)$, $\gamma = 94.123(6)°$, $V = 2138$ Å^3, $Z = 2$, $D_x = 1.985$ g/cm^3, Mo Kα radiation, $\mu = 29.44$ cm^{-1}.

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