Synthetic, Structural and Electrochemical Studies on Some Doubly Bridged Trichalcogen [3.3]Ferrocenophanes‡

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The novel doubly bridged trichalcogen compounds 1,2,3,9,11-pentathia-10-selena[3.3](1,1')(2,2')-ferrocenophane **1** and its 1,3,9,11-tetrathia-2,10-diselena analogue have been prepared by disruption of the trisulfur bridges in 1,2,3,9,10,11-hexathia[3.3](1,1')(2,2')ferrocenophane with lithium aluminium hydride followed by reformation of the bridges using selenium dichloride. The crystal structure of **1** has been determined and indicates a chair–chair conformation of the trichalcogenide linkages, which is the most populous conformeric form in solution. Electrochemistry of various trichalcogen-bridged metallocenophanes indicates chemical reversibility of their redox changes. One-electron removal of the ferrocene systems is shown to be more difficult on introduction of first, one and then two, trichalcogen bridging groups and redox potentials decrease upon substitution of electron-withdrawing sulfur atoms for less withdrawing selenium atoms.

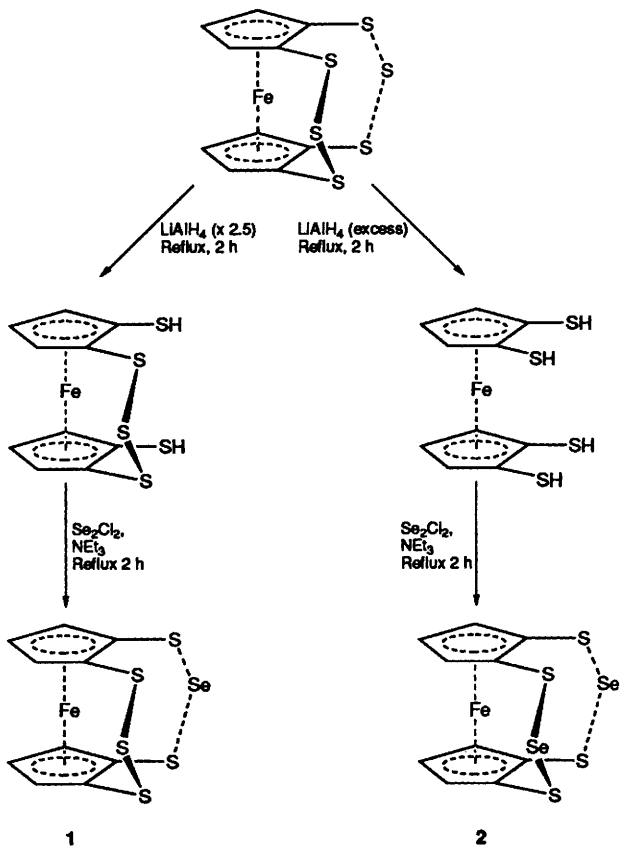
Much of the work in the area of formation of metallocenophanes has concentrated upon the use of methylene units as the bridging species, however, the use of inorganic bridging units, such as chalcogens[1–6] has also yielded much interest. Singly bridged trichalcogen [3]metallocenophanes (where the metal can be iron, ruthenium or osmium) are known[4–10] and have been shown to undergo a restricted bridge reversal.[11] More recently, the synthesis of the first multiply chalcogen-bridged metallocenophanes has been reported.[12,13]

The electrochemistry of singly bridged trichalcogen [3]ferrocenophanes [Fe$(C_5H_4E)_2$E'] has received some attention (E = E' = S;[14–17] E = E' = Se;[16,17] E = E' = Te;[18] E = S, E' = Se;[16,17] E = S, E' = Te;[16] E = Se, E' = S;[17] E = Te, E' = S,[18] E = Te, E' = Se[18]), whereas only a brief report on doubly bridged 1,2,3,9,10,11-hexathia[3.3](1,1')(2,2')ferrocenophane has recently appeared.[13]

We report here the synthetic and electrochemical aspects of the mixed sulfur/selenium doubly bridged species 1,2,3,9,11-pentathia-10-selena[3.3](1,1')(2,2')ferrocenophane **1** and 1,3,9,11-tetrathia-2,10-diselena[3.3](1,1')(2,2')ferrocenophane **2**, and the crystal-structure determination of compound **1**. A detailed electrochemical study of 1,2,3,9,10,11-hexathia[3.3]-(1,1')(2,2')ferrocenophane **3** is also reported.

Results and Discussion

Synthesis.—Following the characterisation of ferrocenophane **3**,[12] our interest has concentrated on the co-ordination chemistry of this multidentate ligand system [some novel copper(I) complexes of **3** have been reported elsewhere[19]] and on the formation of species featuring different bridgehead atoms. In this respect, initial studies have affected a straightforward replacement of the bridgehead sulfurs by selenium atoms and this process is illustrated in Scheme 1. The trichalcogen bridges of **3** are disrupted by addition of lithium aluminium hydride to give a dithiol- or tetrathiol-intermediate. Immediate addition of selenium dichloride (due to the instability of the intermediates) results in a re-formation of the bridges with incorporation of one or two selenium atoms giving compounds **1** and **2** respectively.



Scheme 1

Orange-red **1** was obtained in a yield of 46%, whilst red **2** was isolated in 35% yield. Both compounds were purified by thin layer chromatography on silica and were air- and moisture-stable. For their characterisation, analytical, mass and NMR spectroscopic data were obtained, in addition to the crystal structure determination of **1**.

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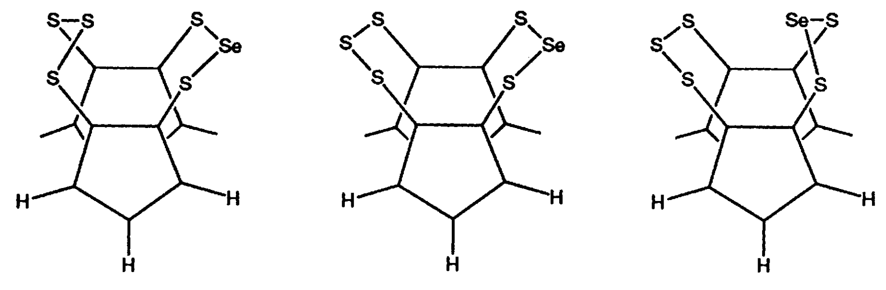
‡ *Supplementary data available*: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

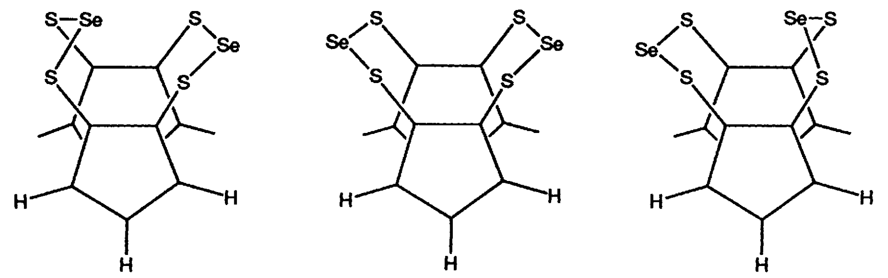
The 'phane' names are based upon a proposal by F. Vögtle and P. Neumann, *Tetrahedron*, 1970, **26**, 5847.

1



boat–chair (26.0%) chair–chair (62.5%) chair–boat (11.5%)

2



boat–chair (35.0%) chair–chair (30.0%) chair–boat (35.0%)

Fig. 1 Solution conformers of 1 and 2

The routes *via* the thiols give great scope for the introduction of various bridgehead moieties, *e.g.* PR, CR_2, SiR_2 (R = H, aryl or alkyl), and investigations along these lines are underway. Particular interest is being focussed on the introduction of transition metals to yield homo- and hetero-bimetallic systems.[20]

Proton NMR studies of compounds **1** and **2** indicate the existence of a number of conformers (Fig. 1). For example, **1** shows evidence for the presence of three individual conformers. As is to be expected from the solid-state structure, the preferred conformer is the chair–chair (62.5%), and the boat–chair (26%) and chair–boat (11.5%) are less favoured. However for **2**, with two SSeS bridges, the two equivalent chair–boat conformers dominate, suggesting that non-bonding interactions between the bridges and the cyclopentadienyl rings are most effectively accommodated in this structural form. Detailed and dynamic NMR studies of compounds **1**–**3** are discussed elsewhere.[21]

Crystal Structure Determination.—The crystal and molecular structure of compound **1** was determined by X-ray diffraction techniques. Its molecular structure is shown in Fig. 2 while selected bond parameters are listed in Table 1. The structure confirms the NMR results, showing that the trichalcogenide linkages adopt the chair–chair conformation. In solution this conformation is the most populous. The two cyclopentadienyl rings adopt an eclipsed conformation and are essentially parallel. The C–C distances in the cyclopentadienyl rings lie in the range 1.40(2)–1.48(2) Å whilst the C–C–C angles range from 106.1(10) to 110.9(11)°. Both parameters compare favourably with analogous ferrocenyl complexes,[4,7,12] as do the Fe–C distances [2.022(12)–2.060(12) Å]. Differences in the ferrocenyl exocyclic C–S–S bond angles [*e.g.* C(5)–C(1)–S(2) 120.9(10) and C(1)–C(5)–S(5) 126.3(9)°] are observed, and this asymmetry is a structural feature common to [3.3]metallocenophanes of this type.[5]

In the molecular structure the Se atom is disordered over the central site on both trichalcogenide linkages, so that Se(1) and S(1) occupy the central position in one chain and S(4) and Se(2) in the other. In the refinement the best results were achieved with the occupancies of 57% for Se(1) and S(4) and 43% for Se(2) and S(1).

Table 1 Bond lengths (Å) and angles (°) for compound **1**

Fe–C(10)	2.022(12)	Fe–C(6)	2.036(11)
Fe–C(1)	2.044(11)	Fe–C(5)	2.050(11)
Fe–C(3)	2.051(11)	Fe–C(9)	2.060(12)
Fe–C(2)	2.067(11)	Fe–C(8)	2.07(2)
Fe–C(7)	2.069(14)	Fe–C(4)	2.072(12)
C(1)–C(2)	1.41(2)	C(1)–C(5)	1.48(2)
C(1)–S(2)	1.751(12)	C(2)–C(3)	1.40(2)
C(3)–C(4)	1.43(2)	C(4)–C(5)	1.45(2)
C(5)–S(5)	1.739(12)	C(6)–C(10)	1.41(2)
C(6)–C(7)	1.43(2)	C(6)–S(3)	1.754(13)
C(7)–C(8)	1.43(2)	C(8)–C(9)	1.41(2)
C(9)–C(10)	1.42(2)	C(10)–S(6)	1.778(13)
Se(1)–S(3)	2.166(4)	Se(1)–S(2)	2.180(4)
S(4)–S(6)	2.153(4)	S(4)–S(5)	2.154(4)
C(2)–C(1)–S(2)	131.3(10)	C(5)–C(1)–S(2)	120.9(10)
C(2)–C(3)–C(4)	110.9(11)	C(3)–C(2)–C(1)	108.4(11)
C(4)–C(5)–C(1)	106.9(10)	C(3)–C(4)–C(5)	106.1(10)
C(1)–C(5)–S(5)	126.3(9)	C(4)–C(5)–S(5)	126.7(8)
C(10)–C(6)–C(7)	106.8(12)	C(10)–C(6)–S(3)	124.8(9)
C(7)–C(6)–S(3)	128.4(10)	C(6)–C(7)–Fe	68.4(7)
C(6)–C(7)–C(8)	108.4(12)	C(9)–C(8)–C(7)	107.6(12)
C(10)–C(9)–C(8)	107.8(13)	C(6)–C(10)–C(9)	109.3(12)
C(6)–C(10)–S(6)	122.6(9)	C(9)–C(10)–S(6)	128.1(10)
C(1)–S(2)–Se(1)	102.2(4)	S(3)–Se(1)–S(2)	101.44(14)
S(6)–S(4)–S(5)	102.2(2)	C(1)–S(2)–S(1)	102.2(4)
C(10)–S(6)–S(4)	102.1(4)	C(6)–S(3)–Se(1)	103.2(4)
C(2)–C(1)–C(5)	107.7(10)	C(5)–S(5)–S(4)	102.9(4)

Electrochemistry.—Fig. 3 compares the cyclic voltammetric response of the all-sulfur doubly bridged complex **3** with that of

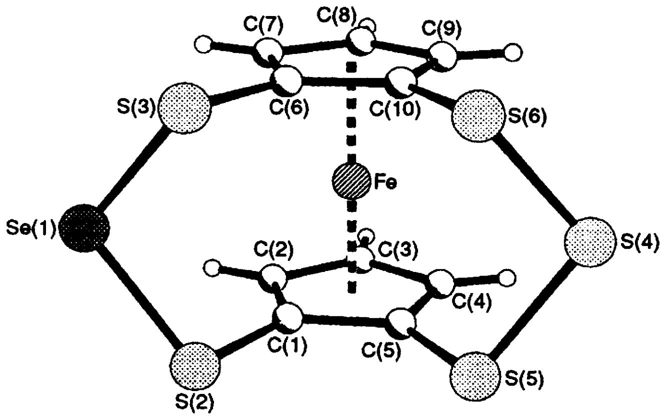


Fig. 2 Molecular structure of compound **1** showing the chair–chair conformation of the trichalcogenide linkages. Only one arrangement of the disordered Se and S atoms are shown

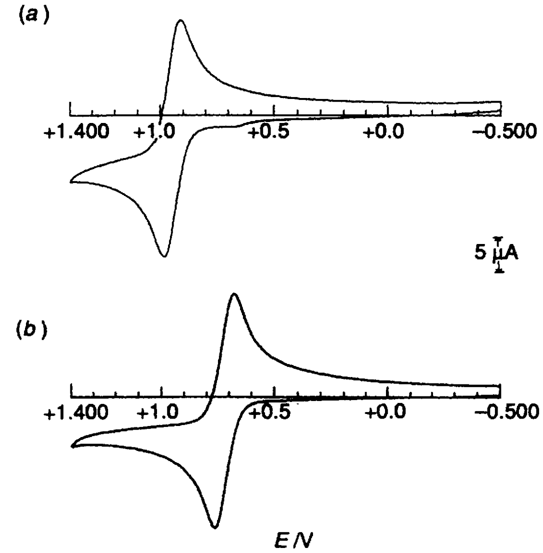


Fig. 3 Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4][ClO_4]$ (0.2 mol dm^{-3}) and: (*a*) **3** (1.5×10^{-3} mol dm^{-3}); (*b*) **4** (1.2×10^{-3} mol dm^{-3}). Scan rate 0.1 V s^{-1}

the related singly bridged 1,2,3-trithia[3](1,1′)ferrocenophane **4** in dichloromethane solution.

Controlled potential coulometric tests on solutions of either **3** ($E_w = +1.05$ V) or **4** ($E_w = +0.9$ V) indicate that the oxidation step involves the consumption of one electron per molecule. Cyclic voltammetry on the exhaustively oxidised solutions affords profiles quite complementary to those shown in Fig. 3, thus pointing out the chemical reversibility of the two redox changes $\mathbf{3}/\mathbf{3}^+$ and $\mathbf{4}/\mathbf{4}^+$, respectively.

Analysis[22] of the cyclic voltammetric responses exhibited by the two complexes with scan rates varying from 0.02 to 2 V s^{-1} indicates that the one-electron oxidation is substantially reversible also from the electrochemical viewpoint, in that: (*i*) the current ratio i_p(backward)/i_p(forward) is constantly equal to 1; (*ii*) the current function i_p(forward)/$v^{\frac{1}{2}}$ remains constant; (*iii*) the peak-to-peak separation is between 70 and 90 mV in the scan rate range 0.02–0.2 V s^{-1}, then progressively increases up to 160 mV at 2 V s^{-1}, likely because of some uncompensated solution resistances. This trend in peak-to-peak separation parallels what we obtained under the same experimental conditions on unsubstituted ferrocene. This suggests that upon one-electron removal no gross structural variation should occur in these trithia ferrocenophane complexes.

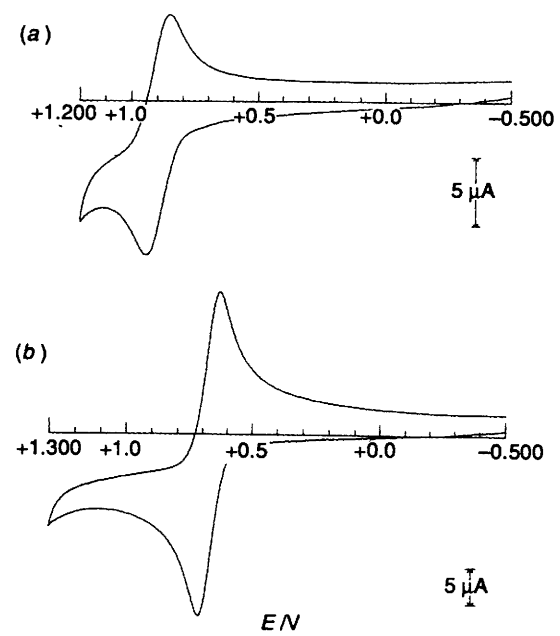


Fig. 4 Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions containing $[NBu_4][ClO_4]$ (0.2 mol dm^{-3}) and: (*a*) **1** (6×10^{-4} mol dm^{-3}); (*b*) **5** (1.1×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}

Table 2 Formal electrode potentials (in V, *vs.* SCE) and peak-to-peak separations (in mV) for the one-electron oxidation of a series of trichalcogen ferrocenophanes in CH_2Cl_2 solution and related complexes

Complex	$E^{\circ\prime}(0/+)$	ΔE_p[a]	Ref.
1 $[Fe\{[C_5H_3(S_3)][C_5H_3(S_2Se)]\}]$	+0.90	84	This work
2 $[Fe\{[C_5H_3(S_2Se)]_2\}]$	+0.93	84	This work
3 $[Fe\{[C_5H_3(S_3)]_2\}]$	+0.95	72	This work
	+0.91	—	13
4 $[Fe\{(C_5H_4)_2S_3\}]$	+0.72	80	This work
	+0.76	—	13
	+0.85		14, 15
5 $[Fe\{(C_5H_4)_2S_2Se\}]$	+0.68	70	This work
6 $[Fe\{(C_5H_4)_2Se_3\}]$	+0.64	70	This work
7 $[Fe\{[C_5H_3(CH_2)_3]_2\}]$	+0.23[b,c]	—	23
8 $[Fe\{(C_5H_4)_2(CH_2)_3\}]$	+0.39[c]	—	24
	+0.31[b,c]	—	23
$[Fe(C_5H_5)_2]$	+0.44	90	This work

[a] Measured at 0.1 V s^{-1}. [b] In MeCN solution. [c] Converted to SCE.

As illustrated in Fig. 4, the cyclic voltammetric responses of the mixed-chalcogen doubly bridged complex **1** and that of the singly bridged 1,3-dithia-2-selena[3](1,1′)ferrocenophane **5** exhibit features qualitatively similar to those of the previous species **3** and **4**.

Also in this case, controlled potential coulometry coupled to cyclic voltammetry proves that these redox changes involve chemically as well as electrochemically reversible one-electron oxidations.

Finally, an analogous redox behaviour has been found for the mixed-chalcogen doubly bridged complex **2** as well as the singly bridged 1,2,3-triselena[3](1,1′)ferrocenophane **6**.

Table 2 summarises the electrochemical parameters for the discussed redox changes.

In agreement with previous findings,[14–17] the presence of one trichalcogen bridge connecting the two cyclopentadienyl rings of ferrocene makes the one-electron removal more difficult by about 300 mV with respect to unsubsituted ferrocene. The introduction of a second trichalcogen bridging group further raises the redox potential by about 200 mV, thus indicating that the effects played by the two S_3 bridges are not simply additive.

It can be also seen that the redox potentials for the singly bridged trichalcogen[3]ferrocenophanes **4**–**6** decrease upon progressive substitution of electron-withdrawing sulfur atoms for less withdrawing selenium atoms, but this trend is not completely maintained in the case of the doubly-bridged trichalcogen[3.3]ferrocenophanes on passing from **1** to **2** and **3**.

Finally, it is noteworthy to look at the significant difference in redox potentials between the trithia-bridged complexes **3** and **4** and the corresponding trimethylene-bridged complexes [3.3]-(1,1′)(2,2′)ferrocenophane **7**[23] and [3](1,1′)ferrocenophane **8**.[23,24] In confirmation of the electron-donating ability of the trimethylene unit against the electron-withdrawing property of the trithia unit, the oxidation potential progressively lowers upon progressive insertion of trimethylene chains.

Experimental

General.—All preparations were carried out using standard Schlenk techniques.[25] All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen.

Proton NMR spectra were recorded on a Bruker AM-400 spectrometer, operating at 400 MHz. The spectra were recorded as $CDCl_2CDCl_2$ solutions with the ^1H chemical shifts being quoted relative to $SiMe_4$ as internal standard. Mass spectra were recorded on a Kratos Profile spectrometer using the electron impact ionisation mode. Elemental analysis was performed in the Department of Chemistry, University of Cambridge.

The preparation of compound **3** has been described previously.[12]

Preparation of 1,2,3,9,11-*Pentathia*-10-*selena*[3.3](1,1′)(2,2′)-*ferrocenophane* **1**.—Compound **3** (0.45 g, 1.20 mmol) was dissolved in diethyl ether (100 cm^3) and lithium aluminium hydride (0.12 g, 3.16 mmol) added to the pale yellow solution. The suspension was refluxed for 3 h and then added to oxygen-free ice-cold water (100 cm^3) containing potassium hydroxide (*ca.* 4 g). Immediately on shaking, a colourless ether layer and a dark red aqueous layer were formed. This latter layer was extracted with diethyl ether (2 × 50 cm^3) and then acidified with hydrochloride acid (*ca.* 5 cm^3) until a grey-green suspension was permanently formed. This suspension was extracted back into diethyl ether (200 cm^3) to give an orange solution which was evaporated to dryness to give a very air-sensitive orange solid (the dithiol intermediate, Scheme 1) (0.28 g, 68%).

The dithiol was dissolved in benzene (100 cm^3) and selenium dichloride (0.19 cm^3, 2.8 mmol) added giving an orange-red suspension. Triethylamine (0.66 cm^3, 5.75 mmol) was added and the suspension refluxed for 2 h. The mixture was filtered and the resultant red-brown solution evaporated to dryness. The crude solid was then subjected to thin layer chromatography on silica plates. Using hexane–dichloromethane (3:1) as eluent, an orange band was collected and slow removal of solvent *in vacuo* gave orange microcrystals of **1** (0.24 g, 46%), m.p. 200–205 °C (decomp.) (Found: C, 28.2; H, 1.3%; M^+ 421. $C_{10}H_6FeS_5Se$ requires C, 28.5; H, 1.4%; *M* 421); *m*/*z* 423 (M^+, 100%).

Crystals for X-ray diffraction were grown from slow evaporation of a solution of **1** in hexane–dichloromethane (1 : 1).

Preparation of 1,3,9,11-*Tetrathia*-2,10-*diselena*[3.3](1,1′)-(2,2′)*ferrocenophane* **2**.—This compound was prepared in an analogous fashion to that described for **1**, except that excess lithium aluminium hydride (0.32 g, 8.4 mmol) was used. Orange-red **2** was isolated in 35% yield, m.p. 190–200 °C (decomp.) (Found: C, 25.7; H, 1.2%, M^+ 470. $C_{10}H_6FeS_4Se_2$ requires C, 25.6; H, 1.3%; *M* 470).

X-Ray Analysis of Compound **1**.—Suitable single crystals of **1** were obtained by slow evaporation of a 1:1 hexane–dichloromethane solution. A crystal was glued on to a glass fibre with epoxy resin and transferred to a Siemens R3mV diffractometer.

Crystal data. $C_{10}H_6FeS_5Se$, $M = 421.28$, monoclinic, space group $P2_1/n$ (alternative setting of $P2_1/c$, no. 14), $a = 6.864(3)$, $b = 11.511(6)$, $c = 15.963(6)$ Å, $\beta = 94.45(3)°$, $U = 1257.5(10)$ Å^3 (by least-squares refinement of diffractometer angles from 25 automatically centred reflections in the range $20 < 2\theta < 25°$, $\lambda = 0.710\,73$ Å), $T = 290(2)$ K, $Z = 4$, $D_c = 2.225$ Mg m^{-3}, D_m = not measured, $F(000) = 824$. Orange block. Crystal dimensions: 0.25 × 0.32 × 0.40 mm, μ(Mo-Kα) = 2.225 mm^{-1}, $\mu R = 0.79$ (R = average radius of the crystal).

Data collection and processing. Siemens R3mV diffractometer, 96-step ω–2θ scans, scan speed 2.50–19.53° min^{-1}, graphite-monochromated Mo-Kα radiation, 2514 reflections measured ($5.0 \leqslant 2\theta \leqslant 50.0°$, $+h$, $+k$, $\pm l$), 2230 unique ($R_{int} = 0.046$ after semi-empirical absorption correction based on an ellipsoid model and ψ scan data [maximum, minimum transmission 0.811, 0.692]), giving 2229 with $F > 4\sigma(F)$. Three standard reflections were monitored at regular intervals throughout data collection but showed no significant variations in intensity.

Structure solution and refinement. The structure was solved by a combination of direct methods and Fourier-difference techniques. The Se atom was disordered over the central site of both S_3 chains and the atoms Se(1) and S(1) and Se(2) and S(4) were assigned the same positional parameters, respectively, and refined with partial occupancies so that the total occupancies corresponded to the presence of one S and one Se atom. The H atoms were placed in idealised positions and allowed to ride on the relevant C atom with the displacement parameter fixed at 0.08 Å^2. The structure was refined by full-matrix least squares on F^2 with all non-hydrogen atoms assigned anisotropic displacement parameters. A weighting scheme of the form $w^{-1} = [\sigma^2F^2 + (0.1661P)^2 + 7.88P]$ where $P = (F_o^2 + 2F_c^2)/3$ gave a satisfactory agreement analysis. The final converged residuals were $R_1 = 0.082$, $wR_2 = 0.213$ (observed data) and $R_1 = 0.117$, $wR_2 = 0.527$ (all data), goodness-of-fit = 1.042 for 155 refined parameters. A final electron-density difference synthesis showed residual density of 1.138 e Å^{-3} close to the Se atom position. Final atomic coordinates for compound **1** are listed in Table 3. All calculations were performed on a Viglen 486DX33 computer using the SHELXTL PLUS[26] and SHELXL 93[27] program packages.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Table 3 Atomic coordinates (× 10^4) for compound **1**

Atom	*x*	*y*	*z*
Fe	1187(2)	1471(1)	8626(1)
C(1)	3932(16)	2169(11)	8669(8)
C(2)	3862(18)	1327(11)	9307(7)
C(3)	3320(18)	262(11)	8932(9)
C(4)	3051(18)	374(10)	8039(8)
C(5)	3434(16)	1586(9)	7855(7)
C(6)	−731(15)	2785(11)	8788(8)
C(7)	−846(20)	1960(13)	9450(9)
C(8)	−1352(23)	854(13)	9084(9)
C(9)	−1619(17)	1008(12)	8204(10)
C(10)	−1224(17)	2188(10)	8027(8)
Se(1)*	2576(2)	4315(1)	9608(1)
S(1)*	2576(2)	4315(1)	9608(1)
S(2)	4541(4)	3646(3)	8713(2)
S(3)	−205(5)	4274(3)	8866(2)
Se(2)*	479(3)	1795(2)	6330(1)
S(4)*	479(3)	1795(2)	6330(1)
S(5)	3364(5)	2228(3)	6867(2)
S(6)	−1348(5)	2890(3)	7032(2)

* The pairs of atoms occupy the same site.

Electrochemistry.—Material and apparatus for electrochemical experiments have been described elsewhere.[18] All the potential values are referred to the saturated calomel electrode (SCE).

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