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SYNTHETIC AND STRUCTURAL STUDIES ON SOME [3]FERROCENOPHANES WITH TRICHALCOGEN BRIDGES. CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-DITHIA-2-SELENA-[3]FERROCENOPHANE

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Summary

A series of [3] ferrocenophanes with the symmetrical trichalcogen chains: —Se_3—, —SSeS—, —STeS—, —SeSSe—, —SeTeSe—, as bridging groups has been synthesized. In solution these compounds are fluxional by a bridge-reversal process. The crystal structure of 1,3-dithia-2-selena-[3]ferrocenophane, which is isomorphous with that of the known 1,2,3-trithia-[3]ferrocenophane, has been determined to assess the effect on molecular geometry of replacement of the central S by Se. Expansion of the bridgehead bonds from S—S 2.049(4) Å to S—Se 2.195(3) Å is compensated by a contraction of the bridgehead valence angle from S—S—S 103.9(2)° to S—Se—S 100.5(1)°, and by an outward displacement of the S atoms by 0.04 Å from the cyclopentadienyl ring planes. Intramolecular repulsions involving Se and adjacent non-bonded ring carbon atoms lead to enhanced asymmetry of the exocyclic C—C—S valence angles, which have mean values of 123.4(4)° and 128.2(4)° compared with 124.0(9)° and 127.1(10)° in the trithia compound. Crystals of the title compound have space group $P2_1/c$ with $a = 9.683(3)$, $b = 9.364(3)$, $c = 11.609(4)$ Å, $\beta = 95.61(2)°$, and $Z = 4$. Least-squares refinement gave $R = 0.038$ for 1408 unique observed reflections whose intensities were measured by counter diffractometry with Mo-K_α radiation.

Introduction

Although a considerable number of [2]- and [3]-ferrocenophanes are known, examples in which only atoms other than carbon are involved in the bridge are

Fig. 1. Bridge-reversal in [3]ferrocenophanes.

relatively few in number. As part of a study [1,2] on ferrocenophanes, we were interested in extending the range of [3]ferrocenophanes to include compounds in which sulphur, selenium and tellurium were the only elements involved in the bridge. One compound of this type, 1,2,3-trithia-[3]ferrocenophane, (Figure 1, X = Y = Z = S) has been reported. [3] It occurred to us that if this class of compound could be extended to include the other chalcogens, then not only could information be obtained about the conformations of the cyclopentadienyl rings in relation to the size of the bridge atoms, but examples would also be provided of organic hetero-trichalcogenides, RXYZR (X, Y, Z = S, Se or Te), a little studied class of compound. [4] In this paper we report on the synthesis of a series of [3]ferrocenophanes with symmetrical trichalcogen chains, and on the crystal and molecular structure of one of these molecules, viz. 1,3-dithia-2-selena-[3]ferrocenophane. Examples of [3]ferrocenophanes with unsymmetrical trichalcogen chains (e.g. Figure 1, X = S, Y = Z = Se) have also been prepared and will be reported on at a later date.

Experimental

^{1}H NMR spectra were recorded at 100 MHz using Jeol MH 100 and PS/PFT 100 spectrometers. Mass spectra were recorded on a V.G. Micromass 16F instrument, and solution molecular weights were measured on a Knauer vapour pressure osmometer. Analyses were obtained from the Exeter University departmental service or from Butterworth Laboratories, Teddington, Middlesex. All solvents were dried and degassed before use, and all reactions were carried out under purified nitrogen. Ferrocene 1,1′-dithiol was prepared by a literature method [3].

1,2,3-Triselena-[3]ferrocenophane

A suspension of 1,1′-dilithioferrocene-bis(*N,N,N′,N′*-tetramethylethylenediamine) in hexane was prepared by stirring for 18 h a mixture of n-butyllithium (269 mmol), ferrocene (20 g, 108 mmol) and *N,N,N′,N′*-tetramethylethylenediamine (40 cm^3, 269 mmol) in hexane (450 cm^3). To this suspension was added selenium powder (34 g, 430 mmol) and the mixture was refluxed for 6 h. To the cooled solution, water (20 cm^3) was added, and the mixture stirred for 30 min. The dark coloured solid was allowed to settle and the supernatant liquid decanted. The solid was extracted with hot hexane until the extracts were colourless. The combined extracts and supernatant liquid were evaporated to dryness, and the solid obtained was dissolved in the minimum amount of dichloromethane and subjected to dry-column chromatography on Grade II alumina. Elution of the column with hexane gave a small amount of ferrocene, followed by a broad red-orange band containing the product, which was crystallized from hexane. Yield 14.2 g (31%). Anal. Found: C, 28.50; H, 1.96; Se, 56.30. Calcd. for $C_{10}H_8FeSe_3$: C, 28.54; H, 1.92; Se, 56.28%.

Further elution with a hexane/benzene (3/1) mixture produced two further bands. Firstly, a band containing bis(ferrocenyl)selenide, crystallized from hexane as pale orange needles. Yield 0.39 g (1.6%), m.p. 163—165° C. Anal. Found: C, 53.55; H, 4.05; Se, 17.36. Calcd. for $C_{20}H_{18}Fe_2Se$: C, 53.50; H, 4.04; Se, 17.59%. ^1H NMR ($CDCl_3$) δ (ppm), 4.14 (4 H, t), 4.18 (10 H, s) 4.32 (4 H, t).

Secondly, a band containing bis(ferrocenyl)diselenide, crystallized from hexane as orange platelets. Yield 0.23 g (0.8%), m.p. 192—195° C. Anal. Found: C, 45.54; H, 3.42; Se, 30.36. Calcd. for $C_{20}H_{18}Fe_2Se_2$: C, 45.50; H, 3.44; Se, 29.91%. ^1H NMR ($CDCl_3$) δ (ppm), 4.20 (10 H, s), 4.36 (8 H, m).

Ferrocene 1,1'-diselenol

1,2,3-triselena-[3]ferrocenophane (2.00 g, 4.8 mmol) was added to a stirred suspension of $LiAlH_4$ (0.45 g, 11.9 mmol) in diethyl ether (100 cm^3). The mixture was refluxed for 2 h, cooled and poured into iced water (100 cm^3). Addition of potassium hydroxide (5 g) produced an orange aqueous layer and a colourless ether layer. The aqueous layer was separated and extracted with ether (2 × 100 cm^3). Acidification of the aqueous layer with concentrated hydrochloric acid (50 cm^3) caused an immediate precipitate of the diselenol, which was extracted into ether (2 × 100 cm^3). The ether was dried over $MgSO_4$, filtered and evaporated to leave the diselenol as air-sensitive orange needles. Yield 1.57 g (95%), m.p. 36—39° C. An analytical sample was prepared by sublimation (0.25 mmHg, 80° C) onto a water cooled probe. Anal. Found: C, 34.85; H, 2.81. Calcd. for $C_{10}H_{10}FeSe_2$: C, 34.92; H, 2.93%.

1,3-Diselena-2-thia-[3]ferrocenophane

Sulphur dichloride (0.15 cm^3, 2.40 mmol) and ferrocene 1,1'-diselenol (0.82 g, 2.0 mmol) were mixed in benzene (100 cm^3). Triethylamine (0.65 cm^3, 4.7 mmol) was then added and the reaction mixture maintained at 50° C for 2 h. The cooled mixture was filtered and the solvent removed from the filtrate to give the crude product, which was purified by dry-column chromatography on Grade II alumina, using hexane for elution and for a final crystallization. Yield 0.52 g (71%). Anal. Found: C, 32.65; H, 2.43. Calcd. for $C_{10}H_8FeSSe_2$: C, 32.11; H, 2.16%.

1,3-Diselena-2-tellura-[3]ferrocenophane

This was prepared from tellurium dichloride (1.03 g, 5.2 mmol), ferrocene 1,1'-diselenol (1.19 g, 3.5 mmol) and triethylamine (1.22 cm^3, 8.8 mmol) in a manner similar to that used for 1,3-diselena-2-thia-[3]ferrocenophane, except that the reaction mixture was refluxed for 1 h and chromatography was omitted. Yield 0.36 g (22%). Anal. Found: C, 25.71; H, 1.64. Calcd. for $C_{10}H_8FeSe_2Te$: C, 25.58; H, 1.72%.

1,3-Dithia-2-tellura-[3]ferrocenophane

This was prepared from tellurium dichloride (0.41 g, 2.1 mmol), ferrocene 1,1'-dithiol (0.39 g, 1.6 mmol) and triethylamine (0.57 cm^3, 3.7 mmol) in a manner similar to that used for 1,3-diselena-2-thia-[3]ferrocenophane, except that the reaction mixture was not heated and chromatography was omitted. Yield 0.18 g (30%). Anal. Found: C, 31.95; H, 2.08; S, 17.13. Calcd. for $C_{10}H_8FeS_2Te$: C, 31.97; H, 2.15; S, 17.06%.

1,3-Dithia-2-selena-[3]ferrocenophane

To a solution of ferrocene 1,1′-dithiol (1.6 g, 6.6 mmol) in ethanol (100 cm^3) was added a solution of sodium ethoxide, prepared from sodium (0.5 g, 21.7 mmol) in ethanol (50 cm^3). Selenium powder (3.5 g, 4.4 mmol) was added and the mixture refluxed for 1 h. Water (5 cm^3) was added to the cold mixture and, after stirring for 15 min, the solvent was evaporated. The residual solid was extracted with hot hexane (2 × 200 cm^3), the extracts dried over $MgSO_4$, filtered and the solvent removed to yield the crude product. Dry-column chromatography on Grade II alumina and elution with hexane gave a single band containing the product, which was crystallized from hexane. Yield 0.83 g (39%). Anal. Found: C, 36.68; H, 2.40; S, 20.28; Se, 23.90. Calcd. for $C_{10}H_8FeS_2Se$: C, 36.72; H, 2.47; S, 19.60; Se, 24.14%.

Reaction of ferrocene 1,1′-dithiol and tellurium tetrachloride

This reaction was carried out in a manner similar to that used for the preparation of 1,3-dithia-2-tellura-[3]ferrocenophane, using the reactants tellurium tetrachloride (0.64 g, 2.4 mmol), ferrocene 1,1′-dithiol (0.96 g, 3.8 mmol) and triethylamine (1.3 cm^3, 9.4 mmol). The only product which could be extracted from the reaction mixture was 1,3-dithia-2-tellura-[3]ferrocenophane, characterized by m.p. and mass spectrum. Yield 0.14 g, (10%).

X-ray crystallography

Crystal data. Crystals suitable for X-ray study were obtained as dark-red needles from hexane solution. Crystal data for the specimen used are given in Table 1. The unit-cell parameters and crystal symmetry were established by a

TABLE 1

CRYSTAL DATA

Molecular formula	$C_{10}H_8FeS_2Se$
Molecular weight	327.12
Space group	$P2_1/c$
a (Å)	9.682(3)
b (Å)	9.364(3)
c (Å)	11.609(4)
β (°)	95.61(2)
U (Å)	1047.5
Z	4
D_x (g cm^{-3})	2.074
$F(000)$	640
λ(Mo-K_α) (Å)	0.71069
μ (cm^{-1})	55.4
Crystal size (mm)	0.30 × 0.18 × 0.20
Crystal forms	$\{101\}$, $\{110\}$, $\{1\bar{1}0\}$
Independent reflections used	1408
2θ max. (°)	50
Scan range (2θ) (°)	2.4—2.7
Scan speed (° min^{-1})	2.93—29.30

least-squares fit to the angular settings for 15 reflections measured using Mo-K_α radiation on a Nicolet P3m automated diffractometer. The crystals are isomorphous with those of 1,2,3-trithia-[3]ferrocenophane, whose structure has been determined by Davis and Bernal [5], and which has cell parameters a = 9.628(3), b = 9.347(4), c = 11.408(4) Å, β = 96.70(3)°, with four molecules in the unit cell. Because of this isomorphism, no measurement of crystal density was made. The volume increment resulting from substitution of S by Se in the bridgehead is 7.0 $Å^3$ mol^{-1}. Confirmation of the space group symmetry comes from observation of systematic absence of reflections $h0l$ with l odd and $0k0$ with k odd.

Intensity data. Intensity measurements were made at room temperature by automatic diffractometry with the θ-2θ scan technique, and with the scan rate dependent on reflection intensity as judged by a 2 s prescan. Background measurements were made at each end of the scan range for a total time equal to that spent on the scan. Mo-K_α radiation was used, made monochromatic by Bragg reflection from a graphite crystal. The intensities of two reference reflections, monitored after every 50 scans, showed an irregular variation of ±2.5% about their mean values over the course of the experiment. No correction was made for absorption, and structure amplitudes and normalized structure amplitudes were derived in the usual ways *.

Structure determination and refinement. Notwithstanding the isostructural character of this material and 1,2,3-trithia-[3]ferrocenophane, its structure was solved independently. The locations of the four heavy atoms were found from an E-map calculated using phases derived for the 196 largest $E(hkl)$. These positions were subjected to six cycles of least-squares refinement (R = 0.23), and the positions of the carbon atoms found from a difference electron-density map (R = 0.14). Refinement by a cascade blocked-matrix least-squares procedure, with anisotropic thermal parameters adopted for the four heavy atoms and individual isotropic thermal parameters used for carbon, reduced R to 0.095, and hydrogen atoms were located from a difference electron-density map. Refinement was continued with all atomic parameters allowed to vary, and with anisotropic thermal parameters used for the non-hydrogen atoms. At convergence $[\Delta(p)/\sigma(p) < 0.04]$, and with a ratio of observations to parameters of 9 : 1, the conventional weighted and unweighted values were 0.037 and 0.038, respectively, for the 1408 independent significant $[I > 2.5\ \sigma(I)]$ reflections used. The weighting factor used in the least-squares procedure was $1/[\sigma^2(F) + gF^2]$ with g set to 0.0012. The scattering factors used were taken from Cromer and Waber [6a], that for hydrogen from Stewart, Davidson and Simpson [7] and that for Se was derived analytically [6b] **. In a final difference electron-density map, none of the residual peaks had structural significance, the largest (+0.7 and —0.75 e) being in the vicinity of the S—Se—S triangle.

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* All crystallographic calculations were carried out on a Data General Eclipse S-230 computer with the SHELXTL Structure Determination Package of Nicolet XRD.

** The Table of structure factors has been deposited with the British Library at Boston Spa, Wetherby LS23 7BQ (Great Britain) as Supplementary Publication No. SUP 90048 (10 pages).

TABLE 2

REACTION YIELDS AND PHYSICAL PROPERTIES OF SOME [3]FERROCENOPHANES

Bridge atoms[a]			Yield (%)	m.p. (°C)	Colour and crystal form	Molecular Weight[b]	^{1}H NMR spectra[c,d,e]			
X	Y	Z					Low temperature limit[f]		High temperature limit[g]	
Se	Se	Se	31	145–147	red-orange needles	424(421)	3.90(m,1) 4.38(m,2) 4.51(m,1)	−19°C	4.11(t,1) 4.31(t,1)	170°C
Se	S	Se	71	148–149	red-orange needles	387(374)	3.90(m,1) 4.42(m,2) 4.51(m,1)	−19°C	4.11(t,1) 4.35(t,1)	161°C
Se	Te	Se	22	180–185 (dec)	bronze platelets	485(470)	4.01(m,1) 4.29(m,1) 4.41(m,1) 4.50(m,1)	−57°C	4.19(t,1) 4.27(t,1)[f]	82°C
S	Te	S	30	180–185 (dec)	bronze platelets	391(376)	3.92(m,1) 4.22(m,1) 4.43(m,1) 4.51(m,1)	−31°C	4.09(t,1) 4.24(t,1)	89°C
S	Se	S	39	145–147	dark-red needles	331(327)	3.81(m,1) 4.32(m,1) 4.44(m,1) 4.52(m,1)	−19°C	4.07(t,1) 4.31(t,1)	167°C

[a] See Fig. 1 for explanation of symbols. [b] Osmometrically in benzene, calculated values in parenthesis. [c] Chemical shifts δ (ppm), δ (TMS) = 0; (multiplicity, relative intensity). [d] m = multiplet, t = unsymmetrical triplet. [e] Spectra recorded at the temperatures shown. [f] $CDCl_3$ solution. [g] $PhNO_2$-d_5 solution.

Results and discussion

1,1′-dilithioferrocene-bis(*N,N,N′,N′*-tetramethylethylenediamine) reacted with elemental selenium in boiling hexane to give predominantly 1,2,3-triselena-[3]ferrocenophane as a red-orange, air-stable, crystalline solid. Small amounts of bis(ferrocenyl)selenide and bis(ferrocenyl)diselenide were also isolated from the reaction mixture. The triselenide was reduced, virtually quantitatively, by $LiAlH_4$ to ferrocene 1,1′-diselenol, which is an air-sensitive, low-melting orange solid. In the ^1H NMR spectrum the diselenol showed unsymmetrical triplets, $\delta = 4.19$ and 4.30 ppm, as expected for the cyclopentadienyl ring hydrogens of a 1,1′-disubstituted ferrocene, together with a triplet, $\delta = 0.90$ ppm, $J(^{77}Se{-}H) = 42.3$ Hz, for the hydrogens attached to selenium. The diselenol and the previously reported [3] corresponding dithiol are important intermediates in the synthesis of the hetero-trichalcogen [3]ferrocenophanes.

1,3-diselena-2-thia-[3]ferrocenophane and 1,3-diselena-2-tellura[3]ferrocenophane were prepared by the reaction of the diselenol, in the presence of triethylamine, with sulphur dichloride and tellurium dichloride, respectively. 1,3-dithia-2-selena-[3]ferrocenophane was prepared by the reaction of the disodium salt of ferrocene 1,1′-dithiol with elemental selenium, and 1,3-dithia-2-tellura-[3]ferrocenophane was prepared by the reaction of ferrocene 1,1′-dithiol, in the presence of triethylamine, with tellurium dichloride. Reaction of the dithiol with tellurium tetrachloride led to reduction of the tellurium and the only product isolated was 1,3-dithia-2-tellura-[3]ferrocenophane.

All the [3]ferrocenophanes are air-stable crystalline solids soluble in organic solvents, and gave satisfactory analytical results. Reaction yields and some physical properties of the [3]ferrocenophanes are listed in Table 2. In the mass spectrometer, the [3]ferrocenophanes show molecular ions and the stepwise loss of

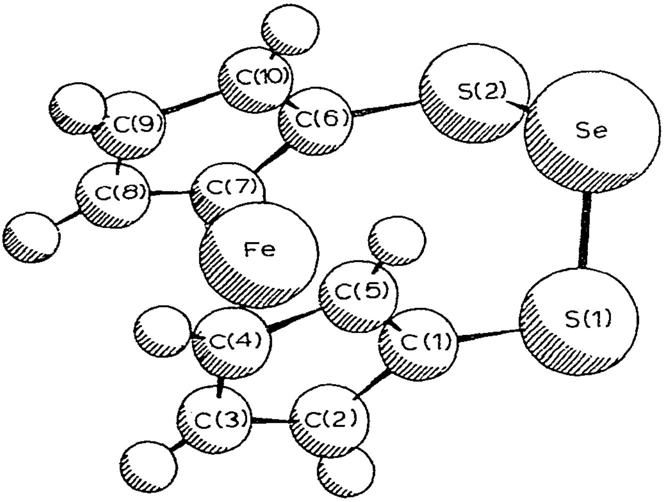

Fig. 2. View of the molecule in the conformation found in the crystal and showing the numbering scheme adopted. Hydrogen atoms, unlabelled in the drawing, are numbered to correspond to the carbon of attachment.

TABLE 3

POSITIONAL AND THERMAL PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS [a,b]

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Se	9866(5)	64 441(6)	7359(4)	488(3)	464(3)	448(3)	151(2)	−135(2)	−37(2)
Fe	28 096(6)	43 901(6)	31 730(5)	304(3)	223(3)	276(3)	−3(2)	20(2)	25(3)
S(1)	18 261(13)	77 150(12)	22 283(11)	467(7)	242(6)	558(7)	52(5)	3(5)	43(5)
S(2)	28 598(15)	52 913(15)	3396(10)	688(9)	470(7)	298(6)	20(5)	91(6)	−39(7)
C(1)	2054(5)	6413(4)	3325(4)	37(2)	25(2)	33(2)	−7(2)	8(2)	4(2)
C(2)	3315(4)	6236(5)	4061(4)	32(2)	34(2)	34(2)	−8(2)	−2(2)	1(2)
C(3)	3081(5)	5125(6)	4852(4)	50(3)	52(3)	27(2)	−4(2)	1(2)	7(3)
C(4)	1716(5)	4601(5)	4583(4)	50(3)	42(3)	35(2)	3(2)	17(2)	3(2)
C(5)	1076(4)	5396(5)	3645(4)	30(2)	39(3)	43(2)	−4(2)	11(2)	3(2)
C(6)	3093(5)	4039(5)	1476(4)	50(3)	30(2)	28(2)	−6(2)	6(2)	4(2)
C(7)	4361(5)	3867(5)	2188(4)	35(2)	40(3)	46(3)	−7(2)	10(2)	7(2)
C(8)	4182(5)	2763(6)	2977(5)	53(3)	38(3)	58(3)	−5(2)	2(2)	23(3)
C(9)	2792(6)	2255(5)	2770(4)	69(3)	20(2)	52(3)	−5(2)	7(3)	4(2)
C(10)	2113(6)	3059(5)	1852(4)	53(3)	24(2)	39(2)	−7(2)	2(2)	−6(2)
H(2)	415(4)	683(5)	409(4)	4(1)					
H(3)	383(6)	492(6)	539(5)	7(1)					
H(4)	134(5)	383(6)	506(4)	5(1)					
H(5)	11(4)	527(4)	328(3)	2(1)					
H(7)	520(4)	428(5)	211(4)	3(1)					
H(8)	501(6)	240(7)	356(5)	3(1)					
H(9)	218(6)	159(6)	318(5)	7(2)					
H(10)	112(5)	293(5)	156(4)	4(1)					

[a] Positional parameters are given as fractions of the unit cell edges, ×10^5 for Se, Fe and S; ×10^4 for C; ×10^3 for H.

[b] Coefficients are given for the exponent in the form $[-2\pi^2(U_{11}h^2a^{*2} + ...2U_{12}hka^*b^* + ...)]$ ×10^4 for Se, Fe and S; ×10^3 for C; ×10^2 for H.

TABLE 4

BOND DISTANCES (Å) [a]

	I [b]	II [c]		I [b]	II [c]
Se—S(1)	2.192(1)	2.202	Se—S(2)	2.198(2)	2.208
S(1)—C(1)	1.761(4)	1.768	S(2)—C(6)	1.763(4)	1.770
C(1)—C(2)	1.430(6)	1.437	C(6)—C(7)	1.421(6)	1.428
C(1)—C(5)	1.418(6)	1.424	C(6)—C(10)	1.419(7)	1.425
C(2)—C(3)	1.421(7)	1.426	C(7)—C(8)	1.403(7)	1.409
C(3)—C(4)	1.416(7)	1.423	C(8)—C(9)	1.425(8)	1.432
C(4)—C(5)	1.412(6)	1.418	C(9)—C(10)	1.414(7)	1.420
Mean	1.419(6)	1.426	*Mean*	1.416(8)	1.423
Fe—C(1)	2.044(4)	2.054	Fe—C(6)	2.042(4)	2.051
Fe—C(2)	2.047(4)	2.056	Fe—C(7)	2.035(5)	2.045
Fe—C(3)	2.060(4)	2.069	Fe—C(8)	2.049(5)	2.059
Fe—C(4)	2.045(5)	2.054	Fe—C(9)	2.053(5)	2.062
Fe—C(5)	2.045(4)	2.055	Fe—C(10)	2.039(5)	2.049
Mean	2.048(6)	2.058	*Mean*	2.044(7)	2.053
C(2)—H(2)	0.98(4)		C(7)—H(7)	0.91(4)	
C(3)—H(3)	0.93(5)		C(8)—H(8)	1.05(5)	
C(4)—H(4)	1.00(5)		C(9)—H(9)	1.01(6)	
C(5)—H(5)	0.99(4)		C(10)—H(10)	0.99(5)	
Mean	0.975(3)		*Mean*	0.99(5)	

[a] E.s.d's, given in parentheses, are applicable to the least significant digits. [b] Uncorrected for thermal motion. [c] Corrected for rigid-body thermal motion.

the Group VI atoms as predominant peaks. The diselenol does not show a molecular ion, the highest peak corresponding to the $(M - 2)^+$ ion. The ^{1}H NMR spectra of the [3]ferrocenophanes are temperature dependent, and at room temperature mostly consist of broad signals. The low temperature limiting spectra (Table 2) are consistent with an ABCD pattern, and the high temperature limiting spectra have a pair of unsymmetrical triplets, characteristic of 1,1′-disubstituted ferrocenes. These spectral properties are consistent with the [3]ferrocenophanes undergoing a bridge-reversal fluxional motion (Figure 1). Detailed studies of the fluxional process in these molecules are being made separately [8], but qualitative observation of the spectra for the different bridging groups indicates an order of activation energies for this motion:

—S$_3$— > —SSeS— > —SeSSe— > —Se$_3$— > —STeS— > —SeTeSe—.

TABLE 5

SELECTED BOND ANGLES (°) [a]

S(1)—Se—S(2)	100.5(1)		
C(1)—S(1)—Se	101.0(1)	C(6)—S(2)—Se	102.6(2)
S(1)—C(1)—C(2)	123.5(3)	S(1)—C(1)—C(5)	128.0(3)
S(2)—C(6)—C(7)	123.4(4)	S(2)—C(6)—C(10)	128.3(4)
C(2)—C(1)—C(5)	108.6(4)	C(7)—C(6)—C(10)	108.2(4)
C(1)—C(2)—C(3)	106.9(4)	C(6)—C(7)—C(8)	107.9(4)
C(2)—C(3)—C(4)	108.4(4)	C(7)—C(8)—C(9)	108.1(4)
C(3)—C(4)—C(5)	108.5(4)	C(8)—C(9)—C(10)	108.2(4)
C(4)—C(5)—C(1)	107.6(4)	C(9)—C(10)—C(6)	107.5(4)

[a] E.s.d's, given in parentheses, are applicable to the least significant digits.

In the solid state, 1,2,3-trithia-[3]ferrocenophane has an eclipsed structure [5], with the cyclopentadienyl rings coplanar with the sulphur atoms in the 1 and 3 positions. An increase in size of the bridging atoms might lead to tilting of the rings away from the bridge, or otherwise alter the molecular conformation. As part of an examination of such effects we have determined the crystal structure of 1,3-dithia-2-selena-[3]ferrocenophane by X-ray diffraction.

Atomic parameters for the crystal structure are given in Table 3. The origin of coordinates chosen in this study is not the same as that selected by Davis and Bernal for the description of 1,2,3-trithia-[3]ferrocenophane [5] and to effect a direct comparison of the atomic coordinates in the two structures the values given by those authors should be transformed to give $x' = 1/2 - x$, $y' = 1/2 + y$, and $z' = 1/2 - z$. A view of the molecule in the conformation found in the crystal, and showing the numbering scheme adopted, is shown in Figure 2. Bond distances calculated from the coordinates in Table 3 are given in Table 4, and bond angles are given in Table 5.

To a reasonable approximation, and ignoring H atoms, the molecule vibrates thermally as a rigid body. The librational, translational and correlation tensors L, S and T [9], describing the motion, are given in Table 6. The generalized goodness of fit residual, Rg, for the observed and calculated orthogonal U_{ij} for the atoms (weighted by atomic number) is 0.062. The centre which yields a symmetric tensor, S, is very close to the geometric centre of the molecule (excluding H atoms) in its x and z components, and is 0.36 Å from that centre in y. The generally good fit of the rigid-body model over all the non-hydrogen atoms suggests that systematic errors caused by neglect of absorption effects may be quite small, and this belief is enhanced by the good internal consistency of bond lengths and angles for chemically equivalent units. Bond distances corrected for the effects of the assumed motion are also given in Table 4.

The values of individual bond distances do not differ significantly from the mean values for the various bond types and are of somewhat higher accuracy than those reported in the earlier analysis of 1,2,3-trithia-[3]ferrocenophane [5], but are in good agreement with them. The S—C distances of 1.761(4) and 1.763(4) Å in the present study compare well with the values of 1.750(9) and 1.763(10) Å found for the trithiane *, as do the mean C—C (1.417(7) vs 1.415-(10) Å) and Fe—C (2.046(7) vs 2.044(10) Å) distances.

As would be expected from the isomorphism of the two unit cells, the changes in molecular geometry and conformation brought about by substitution of S by Se at the bridgehead are quite small. The mean S—Se bond distance of 2.195(3) Å may be compared to the mean S—S distance of 2.049(4) Å found in the trithiane. This lengthening of the bonds from S to the bridgehead atom introduces additional strain into the molecule, and this is relieved in two ways. Firstly, there is a reduction in the valence angle at the bridgehead, from 103.9(2)° for S—S—S to 100.5(1)° for S—Se—S, and, secondly, the two S atoms, which are coplanar with the cyclopentadienyl ring planes in the trithiane, are each displaced outwards from these two planes by 0.04 Å in the present compound. The two C—S—Se angles of 101.9(1)° and 102.6(2)° do not differ significantly from the

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* One of the S—C distances is incorrectly given in the original report as 1.746 Å rather than 1.763 Å, suggesting a spurious degree of internal consistency.

TABLE 6

COMPONENTS OF LIBRATIONAL TENSORS [a]

L(Rad^2)			
	0.0038(2)	0.0001(2)	0.0001(2)
		0.0051(2)	−0.0006(2)
			0.0048(3)
T(Å^2)			
	−0.0236(11)	−0.0001(8)	−0.0007(7)
		0.0212(8)	−0.0019(6)
			0.0270(7)
S(Rad.Å)			
	−0.0008(8)	−0.0004(2)	0.0011(2)
	−0.0004(2)	0.0017(8)	0.0005(3)
	0.0011(2)	0.0005(3)	−0.0009(8)
Centre yielding symmetric S:	0.2557	0.5231	0.2717
Geometric centre (ex H):	0.2590	0.4828	0.2729

[a] E.s.d's, given in parentheses, are applicable to the least significant digit.

C—S—S angles of 102.2(3)° and 103.3(4)°, reported for the trithiane. As a result, the mutual disposition of the two ring planes in the two compounds is hardly changed, with the rings retaining an eclipsed conformation. The mean twist angle between the rings, defined as the mean of torsion angles of the type C(n)—Centroid(1)—Centroid(2)—C(n + 5), is 1.5° in the selenium compound, as compared with only 0.08° in the trithiane. As is also the case in the latter compound, the two ring planes are not quite parallel, the angle between their normals in the selenium compound being 2.4°, compared with 2.9° in the other.

TABLE 7

EQUATIONS OF SELECTED LEAST-SQUARES MEAN PLANES [a]

Cyclopentadienyl ring C(1)—C(5)					
$-0.3299X + 0.5623Y + 0.6727Z = 5.7834$					
Deviations (Å)					
C(1)	+0.007	C(6)	−3.305	S(1)	+0.045
C(2)	−0.009	C(7)	−3.340	Se	−1.589
C(3)	+0.009	C(8)	−3.341	Fe	−1.655
C(4)	−0.005	C(9)	−3.287		
C(5)	−0.001	C(10)	−3.246		
Cyclopentadienyl ring C(6)—C(10)					
$-0.2913X + 0.5714Y + 0.6814Z = 2.6497$					
Deviations (Å)					
C(1)	+3.303	C(6)	−0.010	S(2)	−0.042
C(2)	+3.339	C(7)	+0.007	Se	+1.643
C(3)	+3.347	C(8)	−0.002	Fe	+1.651
C(4)	+3.277	C(9)	−0.005		
C(5)	+3.255	C(10)	+0.009		
Plane Fe, S(1), S(2), C(1), C(6)					
$0.9430X + 0.3180Y + 0.0978Z = 4.1834$					
Deviations (Å)					
C(1)	−0.049	C(6)	−0.032	S(1)	+0.009
C(2)	+1.116	C(7)	+1.139	S(2)	+0.003
C(3)	+0.665	C(8)	+0.739	Fe	+0.011
C(4)	−0.750	C(9)	−0.686	Se	−1.294
C(5)	−1.195	C(10)	−1.162		

[a] $X = x \sin \beta$, $Y = y$, $Z = z + x \cos \beta$.

The tilt of the rings is in the same sense in the two compounds, being roughly about an axis parallel to C(1) ··· C(4) so as to bring C(5) and C(10) into closest contact.

The intramolecular steric repulsions involving Se, C(5) and C(10) cause an asymmetry in the exocyclic valence angles at C(1) and C(6). The mean values for these angles of 123.4(4)° and 128.2(4)° compare with those of 124.0(9)° and 127.1(9)° in the trithiane, suggesting a slightly greater degree of steric repulsion in the Se compound. This is confirmed by comparison of the dihedral angle between the planes Fe—S(1)—S(2) and S(1)—Se—S(2) in this compound, 112.2°, with the corresponding angle in the trithiane, 110.9°. The non-bonded contacts Se ··· C(5) and Se ··· C(10) are 3.510 and 3.555 Å, respectively. If a Van der Waals radius of 1.70 Å is assumed for C, the limiting Van der Waals radius for Se would be between 1.81 and 1.85 Å. This is consistent with the non-bonded Se ··· Se contact of 3.639 Å observed between molecules disposed about the centre of symmetry at the origin of the unit cell. Other intermolecular contacts are of normal Van der Waals type. The packing in the crystal is, of course, the same as that found for 1,2,3-trithia-[3]ferrocenophane, which has been adequately illustrated by Davis and Bernal [5].

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