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SYNTHETIC AND STRUCTURAL STUDIES ON SOME 1,3-DISELENA- AND 1,3-DITHIA-[3]FERROCENOPHANES OF GERMANIUM AND TIN. CRYSTAL AND MOLECULAR STRUCTURE OF 1,3-DISELENA-2,2-DICHLOROGERMYL-[3]FERROCENOPHANE

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Summary

A series of [3]ferrocenophanes of general formula $Fe(C_5H_4X)_2YCl_2$ and the spiro compounds $[Fe(C_5H_4X)_2]_2Ge$ (X = S, Se; Y = Ge, Sn) have been prepared by the reaction of ferrocene 1,1'-dithiol and ferrocene 1,1'-diselenol with tetrahalides of germanium and tin. Spectroscopic properties of the compounds are reported. In solution, the compounds are fluxional by a bridge reversal process. The crystal structure of 1,3-diselena-2,2-dichlorogermyl-[3]ferrocenophane at 163 K has been determined by X-ray diffraction methods. At that temperature, crystals have space group $P2_1/n$ with a 6.222(3), b 16.156(13), c 12.968(4) Å, β 97.53(1)° and $Z = 4$. Least-squares refinement gave $R = 0.033$ for 2834 unique significant reflections whose intensities were measured by counter diffractometry. The two Se–Ge bond lengths are 2.323 and 2.325(1) Å, with Ge–Cl 2.148 and 2.161(1) Å. The Se–Ge–Se bond angle is 118.2(1)°, Cl–Ge–Cl 104.7(1)°, and Se–Ge–Cl angles range from 106.2 to 109.8(1)°. The Se–C bond lengths are 1.901 and 1.904(5) Å, with C–Se–Ge angles of 95.8 and 96.5(2)°. The cyclopentadienyl rings are in an eclipsed conformation with a mean twist angle of 2.7°, and are inclined to one another at 6.1°. The Se atoms are displaced from the ring planes by 0.17 and 0.20 Å yielding a non-bonded intramolecular Se...Se contact of 3.99 Å.

Introduction

We have previously described the synthesis of ferrocene-1,1'-diselenol and its use to synthesize a series of [3]ferrocenophanes with symmetrical trichalcogen chains [1] as well as a series that incorporated a Group IV element at the 2-position in the

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bridge [2]. We have now extended this study to a series of 1,3-dithia- and 1,3-diselena-[3]ferrocenophanes that includes compounds having a germanium or tin atom in the 2-position of the bridge, and in which the Group IV atom is bonded to a potentially reactive functional group, viz. chloride. There are relatively few reports of organosulfur or organoselenium compounds with the Group IV atom bonded to a halogen, and we are interested in such compounds not only as ferrocene derivatives, but also because of their potential use as materials for derivatization of semiconductor electrodes [3]. The crystal and molecular structure of 1,3-diselena-2,2-dichlorogermyl-[3]ferrocenophane at 163 K is reported and comparisons are drawn between that structure and those of other related [3]ferrocenophanes.

Results and discussion

Ferrocene-1,1′-dithiol in hexane, and ferrocene-1,1′-diselenol in diethyl ether, reacted in the presence of triethylamine with a tenfold excess of the tetrahalides of tin and germanium to give good yields of [3]ferrocenophanes (eq. 1):

$$\mathrm{Fe(C_5H_4XH)_2 + YCl_4 + 2Et_3N \rightarrow Fe(C_5H_4X)_2YCl_2 + 2Et_3NHCl} \qquad (1)$$

$(\mathrm{X = S, Se;\ Y = Ge, Sn})$

Analogous reactions with germanium tetrachloride and the ferrocene derivatives in a 1/2 molar ratio yielded the spiro compounds bis(ferrocene-1,1′-dithiolato)germanium(IV) and bis(ferrocene-1,1′-diselenato)germanium(IV). The corresponding spiro compounds of tin have already been reported [2,4]. Attempts to prepare corresponding [3]ferrocenophanes of carbon and silicon by similar methods were frustrated by low reactivity of the Group IV halide in the first case and by high reactivity and instability of the products in the latter case.

All the [3]ferrocenophanes are air-stable crystalline solids, soluble in organic solvents, and gave satisfactory analytical results. These results are listed in Table 1,

TABLE 1

REACTION YIELDS, ANALYTICAL DATA, AND PHYSICAL PROPERTIES OF SOME [3]FERROCENOPHANES

Bridge groups [a]		Yield (%)	M.p. (°C)	Colour	Mass spectrum [b] (calcd.) (abundance) [c]	Analysis (Found (calcd.) (%))		
X	Y					C	H	Cl
S	Ge	61	116–117	orange	392 (392) (41)	30.79 (30.67)	2.24 (2.06)	17.93 (18.11)
S	Sn	62	129–131	dark red	438 (438) (7)	27.81 (27.45)	1.96 (1.84)	15.45 (16.20)
Se	Ge	78	153–155	dark red	486 (486) (50)	24.64 (24.74)	1.78 (1.66)	14.91 (14.61)
Se	Sn	54	124–126	dark red	532 (532) (2)	22.89 (22.60)	1.52 (1.52)	
S	Ge [d]	65	250–265	red	570 (570) (100)	42.37 (42.23)	2.84 (2.83)	
Se	Ge [d]	40	205–210	red	758 (758) (51)	31.57 (31.76)	2.14 (2.13)	

[a] See eq. 1 for explanation of symbols. [b] Base peak of molecular ion. [c] Percentage abundance related to the most abundant ion. [d] Spiro compound.

together with reaction yields and some physical properties of the compounds. In the mass spectrometer the [3]ferrocenophanes all show molecular ions, often as the most abundant species (Table 1), with good agreement of the isotope pattern with theory.

Details of the ^1H NMR spectra of the [3]ferrocenophanes are listed in Table 2. The spectra contain a pair of unsymmetrical triplets in the range δ 4.16 to 4.46 ppm, corresponding to the ferrocenyl protons. These spectral features are similar to those observed for other [3]ferrocenophanes, and have been rationalized in terms of a rapid bridge reversal process [4]. Detailed studies of the process and of the energy barriers involved have been made for a number of [3]ferrocenophanes by variable temperature ^1H NMR [5,6]. Whereas it was possible to obtain low-temperature limiting spectra for some 1,3-dithia-[3]ferrocenophanes, e.g. 1,3-dithia-2-methylene-[3]ferrocenophane [4], it was found that increasing the bridge length resulted in a lower energy barrier to bridge reversal, hence a low-temperature limiting spectrum could not be obtained for 1,3-dithia-2,2-dimethylstannyl-[3]ferrocenophane. Replacement of sulphur by selenium would also be expected to result in lower barriers for the process. Variable temperature ^1H NMR studies were not undertaken on the compounds described here as it was not expected that low temperature limiting spectra would be obtained.

In the ^{13}C NMR spectra (Table 2) the [3]ferrocenophanes show three signals for the cyclopentadienyl carbon atoms. Two of these absorbances, in the range δ 71.3 to 76.2 ppm, are of approximately equal intensity and correspond to the C(2,5) and C(3,4) atoms. The third signal, of low intensity in the range δ 70.1 to 76.0 ppm, is attributable to the C(1) atom. These spectral features are again consistent with a rapid fluxional motion of the bridge.

Atomic parameters for the asymmetric unit of the crystal structure at 163 K of 1,3-diselena-2,2-dichlorogermyl-[3]ferrocenophane are given in Table 3. A view of the molecule, drawn with the program ORTEP [7] and showing the numbering scheme adopted, is shown in Fig. 1. Bond distances, uncorrected for the effects of thermal motion, are given in Table 4, and bond angles are given in Table 5. The thermal motions of all atoms except hydrogen have been treated anisotropically, but because of the nature of the absorption correction applied [8] the results may have limited physical significance.

The two Ge–Se bonds do not differ significantly from their mean value of 2.324(1) Å, though the two Ge–Cl bond lengths do differ significantly from one

TABLE 2

NMR DATA FOR SOME [3]FERROCENOPHANES [a,b,c,d]

Bridge group [a]		^1H Chemical shifts [b,c]	^{13}C Chemical shifts [b]	
X	Y	H(2,3,4,5)	C(1)	C(2,3,4,5)
S	Ge	4.19, 4.41	76.0	75.0, 71.3
S	Sn	4.24, 4.45	75.1	75.4, 71.3
Se	Ge	4.16, 4.46	73.8	75.8, 71.3
Se	Sn	4.16, 4.37	71.3	76.2, 71.4
S	Ge [d]	4.24, 4.35	70.1	75.0, 71.3
Se	Ge [d]	4.22, 4.40	73.8	75.8, 71.3

[a] See eq. 1 for explanation of symbols. [b] δ(ppm), δ(TMS) = 0, $CDCl_3$ solution. [c] Unsymmetrical triplets of equal intensity. [d] Spiro compound.

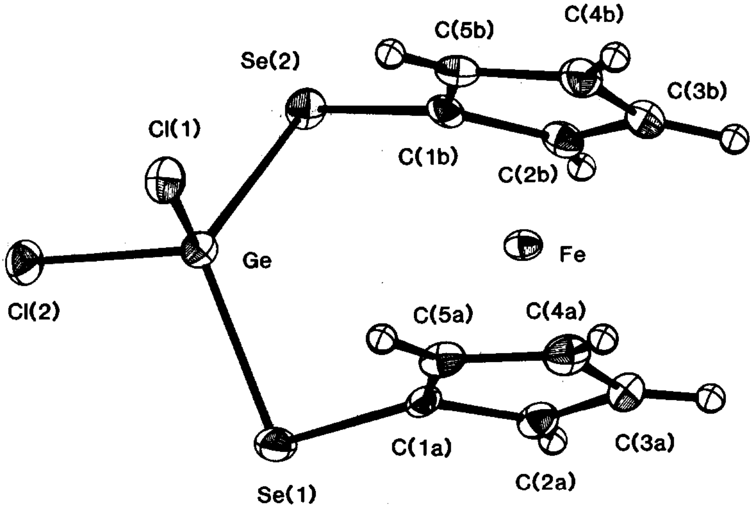

Fig. 1. ORTEP [7] drawing of the molecule of 1,3-diselena-2,2-dichlorogermyl-[3]ferrocenophane, showing the numbering scheme adopted. Hydrogen atoms are numbered to correspond to the carbon of attachment.

TABLE 3

POSITIONAL PARAMETERS WITH THEIR STANDARD DEVIATIONS [a]

Atom	x/a	y/b	z/c
Ge	0.52346(9)	0.27893(3)	0.64917(4)
Se(1)	0.64765(9)	0.17663(4)	0.54578(4)
Se(2)	0.59252(9)	0.26413(3)	0.82877(4)
Fe	0.36409(12)	0.06900(5)	0.73284(5)
Cl(1)	0.18089(22)	0.29895(8)	0.60299(11)
Cl(2)	0.67422(23)	0.39302(9)	0.61293(12)
C(1a)	0.4871(8)	0.0881(3)	0.5947(4)
C(2a)	0.5835(8)	0.0177(3)	0.6486(4)
C(3a)	0.4165(9)	−0.0394(3)	0.6609(4)
C(4a)	0.2179(9)	−0.0043(3)	0.6159(4)
C(5a)	0.2597(8)	0.0743(3)	0.5757(4)
C(1b)	0.4284(8)	0.1653(3)	0.8352(4)
C(2b)	0.5166(8)	0.0898(3)	0.8799(4)
C(3b)	0.3464(9)	0.0335(3)	0.8819(4)
C(4b)	0.1495(9)	0.0728(3)	0.8392(4)
C(5b)	0.1987(8)	0.1550(3)	0.8112(4)
H(2a)	0.736(10)	0.012(4)	0.679(5)
H(3a)	0.435(9)	−0.092(4)	0.693(5)
H(4a)	0.094(8)	−0.030(3)	0.610(4)
H(5a)	0.155(8)	0.111(3)	0.542(4)
H(2b)	0.644(9)	0.079(3)	0.903(4)
H(3b)	0.368(9)	0.048(4)	0.905(4)
H(4b)	0.010(9)	0.048(4)	0.832(5)
H(5b)	0.085(9)	0.194(4)	0.769(5)

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

TABLE 4

BOND DISTANCES (Å) [a]

Ge–Se(1)	2.323(1)	Ge–Se(2)	2.325(1)
Ge–Cl(1)	2.161(1)	Ge–Cl(2)	2.148(1)
Se(1)–C(1a)	1.901(5)	Se(2)–C(1b)	1.904(5)
C(1a)–C(2a)	1.426(7)	C(1b)–C(2b)	1.429(7)
C(1a)–C(5a)	1.421(7)	C(1b)–C(5b)	1.432(7)
C(2a)–C(3a)	1.414(7)	C(2b)–C(3b)	1.398(7)
C(3a)–C(4a)	1.415(7)	C(3b)–C(4b)	1.427(7)
C(4a)–C(5a)	1.411(7)	C(4b)–C(5b)	1.420(7)
Mean	1.417(6)	Mean	1.421(13)
Fe–C(1a)	2.061(4)	Fe–C(1b)	2.050(5)
Fe–C(2a)	2.033(5)	Fe–C(2b)	2.043(5)
Fe–C(3a)	2.030(5)	Fe–C(3b)	2.033(6)
Fe–C(4a)	2.042(5)	Fe–C(4b)	2.042(5)
Fe–C(5a)	2.058(4)	Fe–C(5b)	2.072(5)
Mean	2.045(14)	Mean	2.049(14)
C–H Mean for ring A 0.94(5)		Mean for ring B 0.99(5)	

[a] E.s.d.'s, given in parentheses, are applicable to the least significant digits. Values are uncorrected for the effects of thermal motion.

another. This difference may be attributable to differing thermal motions of the chlorines, but there are also significant differences in the Se–Ge–Cl bond angles, so that it may be due to valence effects at Ge. Both Ge–Cl bond lengths are at the upper end of the range of those reported for simple GeX_4 compounds containing chlorine (2.067–2.148(5) Å) [9].

The Se–C bond angles are identical within the limits of error both with one another and with the corresponding Se–C bonds in bis(ferrocene-1,1′-diselenato)tin(IV) (BDT), whose crystal structure at the same temperature we have previously determined [2]. The Ge–Se–C angles of 95.8 and 96.5(2)° may be compared with the Sn–Se–C angles of 98.6 and 99.7(1)° found in BDT. The mean values of C–C and Fe–C bonds are also comparable to those found for BDT.

Equations for selected least-squares mean planes are given in Table 6. The cyclopentadienyl rings are planar, within the limits of error, and adopt an eclipsed

TABLE 5

SELECTED BOND ANGLES (°) [a]

Se(1)–Ge–Se(2)	118.24(3)	Cl(1)–Ge–Cl(2)	104.72(6)
Se(1)–Ge–Cl(1)	109.70(4)	Se(1)–Ge–Cl(2)	107.24(6)
Se(2)–Ge–Cl(1)	109.82(4)	Se(2)–Ge–Cl(2)	106.19(4)
Ge–Se(1)–C(1a)	96.5(2)	Ge–Se(2)–C(1b)	95.8(2)
Se(1)–C(1a)–C(2a)	123.9(4)	Se(2)–C(1b)–C(2b)	123.7(4)
Se(1)–C(1a)–C(5a)	127.9(4)	Se(2)–C(1b)–C(5b)	127.8(4)
C(1a)–C(2a)–C(3a)	107.9(4)	C(1b)–C(2b)–C(3b)	108.2(5)
C(2a)–C(3a)–C(4a)	107.9(4)	C(2b)–C(3b)–C(4b)	108.5(5)
C(3a)–C(4a)–C(5a)	108.7(5)	C(3b)–C(4b)–C(5b)	108.2(5)
C(4a)–C(5a)–C(1a)	107.7(4)	C(4b)–C(5b)–C(1b)	107.2(5)
C(5a)–C(1a)–C(2a)	107.8(4)	C(5b)–C(1b)–C(2b)	108.0(4)

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

TABLE 6

EQUATIONS OF SELECTED LEAST-SQUARES MEAN PLANES [a]

Cyclopentadienyl ring C(1a)–C(5a)

$-0.23104X+0.42194Y+0.87669Z=6.84274$

Deviations (Å)

C(1a)	0.006	C(1b)	−3.410	Ge	−1.878
C(2a)	−0.004	C(2b)	−3.289	Se(1)	0.204
C(3a)	0.001	C(3b)	−3.174	Se(2)	−3.772
C(4a)	0.002	C(4b)	−3.227	Cl(1)	−1.968
C(5a)	−0.005	C(5b)	−3.389	Cl(2)	−2.016

Cyclopentadienyl ring C(1b)–C(5b)

$-0.25170X+0.32345Y+0.91216Z=10.35100$

Deviations (Å)

C(1a)	3.425	C(1b)	0.006	Ge	1.823
C(2a)	3.288	C(2b)	−0.004	Se(1)	3.809
C(3a)	3.176	C(3b)	−0.001	Se(2)	−0.175
C(4a)	3.229	C(4b)	0.005	Cl(1)	1.743
C(5a)	3.372	C(5b)	−0.007	Cl(2)	1.903

Plane Se(1), Se(2), C(1a), C(1b)

$0.79925X-0.47002Y+0.37454Z=3.78600$

Deviations (Å)

C(1a)	−0.023	C(1b)	0.023	Ge	1.057
C(2a)	−1.224	C(2b)	1.143	Se(1)	0.020
C(3a)	−0.869	C(3b)	0.731	Se(2)	−0.019
C(4a)	0.541	C(4b)	0.695	Cl(1)	3.072
C(5a)	1.069	C(5b)	1.171	Cl(2)	1.299

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

conformation with a mean twist angle * of 2.7°. The ring planes are inclined at an angle of 6.1°. The selenium atoms are displaced from the mean planes of the rings to which they are attached by 0.17 and 0.20 Å, yielding a non-bonded Se...Se separation of 3.99 Å, comparable to the 4.00 Å found in BDT, but considerably larger than that found in the structures of several 1,3-diselena-[3]ferrocenophanes we have studied [10]. It does not seem, then, as though the enlarged Se–Ge–Se bond angle of 118.2(1)° (cf. Se–Sn–Se, 108.6(1)°) is attributable to a limiting Se...Se contact.

The asymmetry in the exocyclic valence angles of the rings at C(1), 123.8 vs. 127.8(4)°, is characteristic of [3]ferrocenophanes and indicates strain in the contacts between the ring atoms C(5) and the atom occupying the 2-position in the bridgehead. The Ge...C(5) contacts are 3.69 and 3.76 Å, compared to the sum of the Van der Waals, radii, 3.70 Å. Although only one contact is limiting, the strain appears to be transmitted to the second ring.

The overall molecular geometry is very much like that found in other [3]ferrocenophanes containing chalcogen bridges: in 1,3-dithia-2-selena-[3]ferrocenophane (DSF) [1], 1,2,3-trithia-[3]ferrocenophane (TTF) [11], and BDT [2]; as well as in our

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* Defined as the mean of the torsion angles C(na)–CT(a)–CT(b)–C(nb), where CT(a) and CT(b) are the respective ring centroids.

unpublished structures [10]. A detailed analysis of the stereochemical factors leading to strain in these ferrocenophanes will be given separately [12].

Experimental

^{1}H NMR spectra were recorded at 100 MHz on a Jeol MH 100 spectrometer. Mass spectra were recorded on a V.G. Micromass 16F instrument. Analyses were obtained from Butterworth Laboratories, Teddington, Middlesex, or from C.H.N. Analysis, South Wigston, Leicester. All solvents were dried and degassed before use, and all reactions were carried out under purified nitrogen. Ferrocene-1,1′-dithiol and ferrocene-1,1′-diselenol were prepared by literature methods [1,4]. Petroleum spirit was a 60–80°C boiling fraction.

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

Ferrocene-1,1′-dithiol (0.75 g, 3 mmol) in hexane (50 cm^3) was added dropwise to tetrachlorogermane (3.6 cm^3, 30 mmol) with stirring. Triethylamine (0.84 cm^3, 6 mmol) was added and the mixture stirred for 1 h. The solvent was removed under vacuum and the residue extracted with petroleum spirit until the extracts were colourless, and then extracted with benzene. From the benzene extract a small amount of bis(ferrocene-1,1′-dithiolato)germanium(IV) was obtained. The product was obtained from the petroleum extract, and purified by recrystallization from petroleum spirit. Yield 0.72 g (61%).

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

This was prepared from tin tetrachloride (3.4 cm^3, 30 mmol), ferrocene-1,1′-dithiol (0.75 g, 3 mmol), and triethylamine (0.84 cm^3, 6 mmol) in the same manner as that described for 1,3-dithia-2,2-dichlorogermyl-[3]ferrocenophane. A small amount (0.09 g, 0.15 mmol) of bis(ferrocene-1,1′-dithiolato)tin(IV) was also produced, and the product was obtained as very dark red needles. Yield 0.82 g (62%).

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

This was prepared from tin tetrachloride (2.3 cm^3, 20 mmol), ferrocene-1,1′-diselenol (0.69 g, 2 mmol) in diethyl ether (20 cm^3), and triethylamine (0.56 cm^3, 4 mmol) in a manner similar to that described above. Bis(ferrocene-1,1′-diselenato)tin(IV) (0.20 g, 0.25 mmol) was also produced, and the product was obtained as very dark red crystals. Yield 0.57 g (54%).

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

This was prepared from germanium tetrachloride (2.4 cm^3, 20 mmol), ferrocene-1,1′-diselenol (0.69 g, 2 mmol) in diethyl ether (20 cm^3), and triethylamine (0.56 cm^3, 4 mmol) in the manner described above. The product was obtained as dark red crystals. Yield 0.75 g (78%).

Bis(ferrocene-1,1′-dithiolato)germanium(IV)

Germanium tetrachloride (0.12 cm^3, 1 mmol) in diethyl ether (30 cm^3) was added to a stirred solution of ferrocene-1,1′-dithiol (0.5 g, 2 mmol) in diethyl ether (50 cm^3). Triethylamine (1.40 cm^3, 10 mmol) was then added, and the reaction mixture stirred for 1 h. The solvent was removed under vacuum, and the product was obtained from the residue by extraction with benzene. Yield 0.37 g (65%).

Bis(ferrocene-1,1′-diselenato)germanium(IV)

Germanium tetrachloride (0.12 cm^3, 1 mmol) in hexane (50 cm^3) was added dropwise to a stirred solution of ferrocene-1,1′-diselenol (0.69 g, 2 mmol) in hexane (75 cm^3). Triethylamine (1.40 cm^3, 10 mmol) was then added and the mixture stirred for 2 h. The mixture was filtered and the solvent removed under vacuum to give the crude product, which was then recrystallized from benzene. Yield 0.31 g (40%).

X-ray crystallography

Crystal data. Crystals suitable for X-ray study were obtained by recrystallization from dichloromethane solution as irregular red-brown plates. Crystal data for the specimen used are given in Table 7. The sample was cooled to 163 K by immersion in a stream of cooled N_2 gas by use of the Nicolet LT-1 cooling device. Crystal symmetry and space group were derived from 25° precession photographs taken with Mo-K_α radiation at room temperature. No phase transition is apparent on cooling to the lower temperature. The systematic absences observed were $0k0$ with k odd and $h0l$ with $h+l$ odd. These absences uniquely define the space group as $P2_1/n$, a non-standard setting of $P2_1/c$. Unit cell parameters at 163 K were derived from a least-squares fit to the observed diffractometer setting angles for 15 strong reflections measured with Mo-K_α radiation on the Nicolet P3m automated diffractometer.

Intensity data. Intensity measurements were made for a single quadrant of reciprocal space with the θ–2θ scanning method. The time spent on each measurement was proportional to intensity, scan speeds ranging from 2.93–19.53° min^{-1}. Background measurements were made on either side of the peaks for a total time equal to that spent on the scan. Mo-K_α radiation was used, made monochromatic by Bragg reflection from the (002) planes of a pyrolytic graphite crystal. Scintillation

TABLE 7

CRYSTAL DATA

Molecular formula	$C_{10}H_8Cl_2FeGeSe_2$
Molecular weight	485.4
Temperature (K)	163
Space group	$P2_1/n$
a (Å)	6.222(3)
b (Å)	16.156(13)
c (Å)	12.968(4)
β (°)	97.53(1)
U (Å^3)	1292(4)
Z	4
D_x (g cm^{-3})	2.495
$F(000)$	912
λ(Mo-K_α) (Å)	0.71069
μ (cm^{-1})	100
Crystal size (mm)	0.10×0.30×0.35
Independent reflections used	2834 (82.9% with $I > 2.5\sigma(I)$)
2θ max. (°)	50
Scan range (2θ) (°)	2.62–2.92
Scan speed (° min^{-1})	2.93–19.53

counting was used with pulse-height analysis. The intensities of two reference reflections, measured after every 50 scans showed a random variation of 2.3% about their means. Structure amplitudes were derived in the usual way. The irregular form of the crystal prevented application of a rigorous absorption correction. An empirical correction [8] was applied following isotropic refinement of the structural parameters *.

Structure determination and refinement. The structure was solved without difficulty by the heavy atom method, the positions of the Ge, Se, and Fe atoms being determined from a three-dimensional sharpened Patterson function. Initial refinement of the atomic parameters with isotropic thermal parameters adopted converged at $R = 0.109$, and application of the absorption correction reduced R to 0.078. Hydrogen positions were calculated and least-squares refinement continued with anisotropic thermal parameters adopted for all atoms except hydrogen, for which isotropic thermal parameters were used. Refinement proceeded smoothly and convergence was reached with R 0.033 and $R(\mathrm{w})$ 0.026. The ratio of observations to parameters was 13/1 and the maximum shift/error ratio in the final cycle was 0.02. The weighting factor used was $1/[\sigma^2(F_0) + 0.001\ F_0{}^2]$. Scattering factors for the atoms were taken from [13] and, for Ge, Se, Fe, and Cl, were corrected for the real and imaginary components of anomalous dispersion **.

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* Initial data reduction and subsequent calculations were carried out on an XDS Sigma 2 computer using locally written programs.

** The Table of structure factors and anisotropic thermal parameters has been deposited with the British Library at Boston Spa, Wetherby LS23 7BQ (Great Britain) as Supplementary Publication No. SUP 90099 (19 pages).