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CRYSTAL AND MOLECULAR STRUCTURE OF 1,2,3-TRISELENA[3]RUTHENOCENOPHANE

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Summary

1,2,3-Triselena[3]ruthenocenophane (I) has been prepared by the reaction of 1,1′-dilithioruthenocene with elemental selenium. The crystal structure of the compound I has been determined by X-ray diffraction methods. The crystals have space group $C2/c$ (No. 15) with a 27.470(24), b 5.820(6), c 13.816(12) Å, β 102.17(5)° and $Z = 8$. Least-squares refinement gave $R = 0.074$ for 1289 unique observed reflections whose intensities were measured by counter diffractometry with Mo-K_α radiation. The two Se–Se bond lengths are identical at 2.326 Å and the Se–Se–Se bond angle is 102.15(9)°. The Se–C bond lengths are 1.877(14) and 1.929(15) Å with Se–Se–C bond angles of 100.4(4) and 100.5(5)°. The cyclopentadienyl rings are in an eclipsed conformation and are parallel with an inter-ring separation of 3.65 Å. There are several short Se $\cdots$ Se intermolecular contacts, the shortest being 3.50 Å.

Introduction

Although a number of [3]ferrocenophanes containing trichalcogen bridges have been prepared [1,2] and several of them have been structurally characterised by X-ray diffraction [2–4], the only analogous ruthenium compound to be reported is 1,2,3-trithia[3]ruthenocenophane [5]. In view of the greater ring–ring separation in ruthenocene (3.68 Å) compared with ferrocene (3.32 Å), a point of structural interest is the effect of this increased distance on the bridge geometry in ruthenocenophanes. As far as we are aware only four ruthenocenophanes have been structurally characterised by X-ray diffraction viz., 1,3-(1,1′-ruthenocenediyl)propane [6], 1,4-(1,1′-ruthenocenediyl)butane [6], (η^5,η^5,1,1′-(2,4,4,6-tetrafluorocyclotriphosphazene-2,6-diyl)-bis(cyclopentadienyl))ruthenium [7] and (η^5,η^5,1,1′-(2,4,4,6, 8,8-hexafluorocyclotetraphosphazene-2,6-diyl)bis(cyclopentadienyl))ruthenium [7].

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We now report the crystal and molecular structure of 1,2,3-triselena[3]-ruthenocenophane.

Experimental

All solvents were dried and degassed before use and all reactions were carried out under purified nitrogen. Microanalysis was performed by the Exeter University departmental service.

1,2,3-Triselena[3]ruthenocenophane (I)

A suspension of the *N,N,N',N'*-tetramethylethylenediamine (TMED) adduct of 1,1'-dilithioruthenocene was prepared by adding n-butyllithium (5 mmol) and TMED (0.58 g, 5 mmol) to a solution of ruthenocene (0.46 g, 2 mmol) in hexane (10 cm^3). The mixture was stirred at room temperature for 18 h, then cooled to $-20°C$ and the supernatant liquid removed. Hexane (10 cm^3) was added and the mixture was stirred briefly and again cooled before removing the supernatant liquid. Hexane (10 cm^3) and selenium powder (0.8 g, 10 mmol) were added and the mixture was refluxed for 7 h, then cooled and filtered to remove excess selenium. The filtrate was concentrated and subjected to chromatography on Grade II alumina with hexane as eluant. A colourless band containing ruthenocene was followed by a broad yellow band containing the product, which was crystallised from dichloromethane/hexane (1/1) to yield orange crystals (m.p. 214–216°C), suitable for X-ray studies. Anal. Found: C, 26.35; H, 1.86. $C_{10}H_8RuSe_3$ calcd.: C, 25.77; H, 1.75%.

X-ray crystallography

Crystal data. $C_{10}H_8RuSe_3$. $M = 466.12$, monoclinic, a 27.470(24), b 5.820(6), c 13.816(12) Å, β 102.17(5)°. U 2159(6) Å^3. $Z = 8$. λ (Mo-K_α) 0.71069 Å, μ 113.8 cm^{-1}, D_x 2.868 g cm^{-3}, space group $C2/c$ (No. 15), crystal dimensions $0.5 \times 0.12 \times 0.012$ mm.

Data collection and processing. The crystal was mounted on a STADI-2 diffractometer with the needle axis (b) parallel to the spindle. Cell dimensions were determined from accurate values of ω and 2θ for eight reflections. The relatively high e.s.d.'s may be attributed to the large size and irregular shape of the diffraction spots. Intensities were measured for a total of 1914 independent data to a resolution of 0.84 Å for layers $h0l$–$h6l$. No significant variations were observed in the intensities of two reference reflections measured after each layer. Of the 1914 independent data measured, 1289 with $F > 2\sigma(F)$ were used for the solution and refinement of the structure.

Structure analysis and refinement. The structure was solved using the Patterson and tangent expansion routines of SHELX84 [8]. The structure was refined isotropically by full-matrix least-squares, with hydrogen atoms in fixed idealised positions (C–H 1.08 Å) [9]. When the series had converged, absorption corrections were applied using DIFABS [10]. The maximum and minimum corrections calculated were 0.81 and 1.22. Ruthenium and selenium atoms were then refined anisotropically with $w^{-1} = \sigma^2(F) + 0.00053F^2$. Final values were: $R = 0.074$, $R_w = 0.054$, $S = 1.05$, maximum shift/error in the last cycle was 0.002. A final difference electron density synthesis gave maximum peak and minimum trough of 1.4 and -1.3 e Å^{-3}. Scattering factors were taken from [11] and other computer programs

TABLE 1

FRACTIONAL COORDINATES OF ATOMS WITH STANDARD DEVIATIONS

Atom	x	y	z	U_{eq} ^{a}
Ru	0.09177(5)	0.22238(19)	0.04112(8)	0.0223
Se(1)	0.17748(7)	0.3298(3)	0.27268(12)	0.0385
Se(2)	0.23063(6)	0.2524(3)	0.16606(12)	0.0424
Se(3)	0.20680(7)	0.5281(3)	0.04328(12)	0.0396
C(1)	0.1184(5)	0.1965(25)	0.2021(10)	0.0270
C(2)	0.0712(5)	0.3103(25)	0.1808(10)	0.0268
C(3)	0.0362(6)	0.153(3)	0.1286(11)	0.0321
C(4)	0.0591(6)	−0.050(3)	0.1150(11)	0.0346
C(5)	0.1101(5)	−0.0243(23)	0.1632(9)	0.0212
C(6)	0.1452(6)	0.397(3)	−0.0283(10)	0.0316
C(7)	0.0996(5)	0.5194(25)	−0.0514(9)	0.0258
C(8)	0.0633(7)	0.370(3)	−0.1058(11)	0.0374
C(9)	0.0879(6)	0.159(3)	−0.1167(11)	0.0338
C(10)	0.1377(6)	0.171(3)	−0.0688(10)	0.0311

^{a} $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$.

used were CALC [12], ORTEPII [13], and PLUTO [14]. Final positional parameters for the non-hydrogen atoms are listed in Table 1. Tables of observed and calculated structure factors, anisotropic thermal parameters, hydrogen atom parameters and selected torsion angles have been deposited *.

Results and discussion

A view of the molecule showing the numbering scheme adopted is shown in Fig. 1. In Tables 2 and 3 are listed the internuclear separations and interbond angles respectively for all non-hydrogen atoms. In the crystal, molecules of I occupy

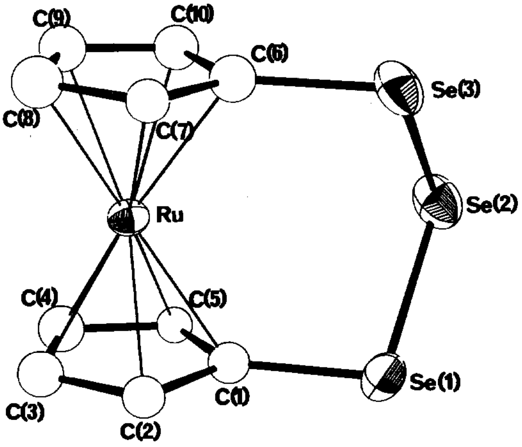

Fig. 1. ORTEP drawing of the molecule showing the numbering scheme adopted.

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* British Library at Boston Spa, Wetherby LS23 7BQ (Great Britain). Supplementary Publication No. SUP 90123 (11 pages).

TABLE 2

INTERATOMIC DISTANCES (Å)

Ru–C(1)	2.194(14)	Se(1)–C(1)	1.877(14)
Ru–C(2)	2.183(14)	C(1)–C(2)	1.431(20)
Ru–C(3)	2.175(16)	C(1)–C(5)	1.393(20)
Ru–C(4)	2.179(16)	C(2)–C(3)	1.411(21)
Ru–C(5)	2.192(14)	C(3)–C(4)	1.370(22)
Ru–C(6)	2.167(15)	C(4)–C(5)	1.427(21)
Ru–C(7)	2.187(14)	Se(3)–C(6)	1.929(15)
Ru–C(8)	2.191(16)	C(6)–C(7)	1.417(21)
Ru–C(9)	2.192(16)	C(6)–C(10)	1.431(21)
Ru–C(10)	2.189(15)	C(7)–C(8)	1.414(21)
Se(1)–Se(2)	2.3263(25)	C(8)–C(9)	1.424(23)
Se(2)–Se(3)	2.3265(25)	C(9)–C(10)	1.389(22)

general positions, although within experimental error the molecule has C_s symmetry, with a mirror plane passing through Se(2) and Ru, normal to the line joining the centroids X(1) and X(2) of the cyclopentadienyl rings. The mean C–C bond length is 1.411(21) Å and the mean C–C–C angle is 108.0(18)°. Mean bond distances from Ru to C are 2.185(15) Å; these compare with 2.21 Å in ruthenocene [15]. The separation X(1)–X(2) is 3.65 Å, compared with 3.68 Å in ruthenocene [15].

The two Se–Se bond lengths are not significantly different from one another nor from the overall average of Se–Se distances, 2.334 Å, found in elemental selenium [16]. The Se–Se–Se angle of 102.5° compares with the value of 100.7° for the corresponding angle in the analogous ferrocenophane [4]. This difference is presumably accounted for by the greater inter-ring separation in the ruthenocene derivative. That the wider angle in I represents a reduction in bond angle strain is also indicated by the fact that whilst the Se–Se–C angles in the iron analogue are unequal, 98.2(2) and 99.7(3)°[4], in I they are essentially identical, 100.4(4) and 100.5(5)°.

Equations for selected least-squares mean planes are given in Table 4. The cyclopentadienyl rings are planar and adopt an eclipsed conformation with a twist of the rings, defined as the mean value of the torsion angles C(n)–X(1)–X(2)–C(n + 5), of 1.0(13)°. The selenium atoms are displaced from the ring to which they are attached by 0.01 and 0.05 Å, giving an intramolecular non-bonded Se ··· Se separation of 3.620(3) Å.

TABLE 3

SELECTED INTERBOND ANGLES (°)

Se(1)–Se(2)–Se(3)	102.15(9)	Se(2)–Se(3)–C(6)	100.5(5)
Se(2)–Se(1)–C(1)	100.4(4)	Se(3)–C(6)–C(7)	123.8(11)
Se(1)–C(1)–C(2)	124.3(11)	Se(3)–C(6)–C(10)	127.1(11)
Se(1)–C(1)–C(5)	129.4(11)	C(7)–C(6)–C(10)	109.1(13)
C(2)–C(1)–C(5)	106.3(12)	C(6)–C(7)–C(8)	107.5(13)
C(1)–C(2)–C(3)	107.1(13)	C(7)–C(8)–C(9)	106.8(14)
C(2)–C(3)–C(4)	110.4(14)	C(8)–C(9)–C(10)	110.5(14)
C(3)–C(4)–C(5)	106.2(13)	C(6)–C(10)–C(9)	106.1(13)
C(1)–C(5)–C(4)	110.0(12)		

TABLE 4

EQUATIONS AND DEVIATIONS (Å) OF SELECTED MOLECULAR PLANES

(a) Plane Ru, Se(1), Se(3), C(1), C(6)					
$-13.650x+5.022y+2.693=-0.052$					
Ru	0.027	Se(1)	0.020	Se(3)	−0.002
C(1)	−0.033	C(6)	−0.011		
Se(2)	−1.382	C(2)	1.126	C(3)	0.670
C(4)	−0.698	C(5)	−1.134	C(7)	1.163
C(8)	0.760	C(9)	−0.664	C(10)	−1.156
(b) Plane C(1)–C(5) (cyclopentadienyl ring)					
$-10.562x-1.938y+12.748z=0.952$					
C(1)	−0.008	C(2)	0.000	C(3)	0.009
C(4)	−0.013	C(5)	0.013		
Ru	−1.828	Se(1)	0.011	Se(2)	−1.760
Se(3)	−3.608	C(6)	−3.615	C(7)	−3.666
C(8)	−3.687	C(9)	−3.676	C(10)	−3.613
(c) Plane C(6)–C(10) (cyclopentadienyl ring)					
$-11.462x-1.911y+12.660z=-2.780$					
C(6)	0.000	C(7)	−0.005	C(8)	0.008
C(9)	−0.008	C(10)	0.006		
Ru	1.824	Se(1)	3.568	Se(2)	1.757
Se(3)	−0.051	C(1)	3.614	C(2)	3.661
C(3)	3.692	C(4)	3.667	C(5)	3.618

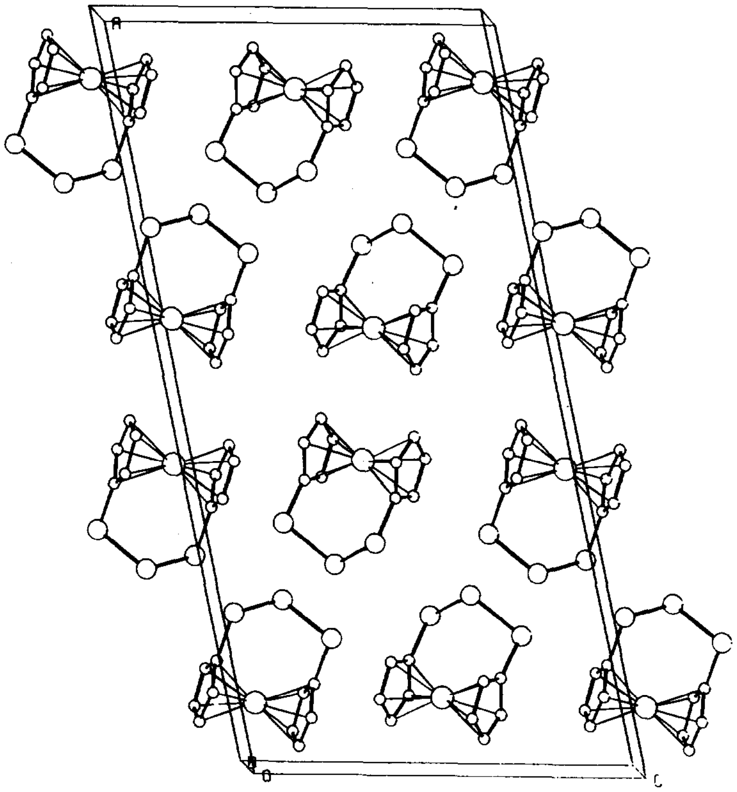

Fig. 2. The packing of the molecule in the crystal.

TABLE 5

SELECTED INTERMOLECULAR CONTACTS

Atom A	Atom B	Symmetry for B	Distance (Å)
Se(1)	Se(2)	$0.5-x, 0.5+y, 0.5-z$	3.498
Se(2)	Se(2)	$0.5-x, 0.5+y, 0.5-z$	3.734
Se(1)	Se(3)	$x, -y, 0.5+z$	3.747
Se(3)	Se(3)	$0.5-x, 0.5-y, -z$	3.864

Asymmetry in the exocyclic bond angles at the bridgehead carbon atoms is a feature of [3]ferrocenophanes in which Group IV atoms are attached to the rings [17] and has been attributed to steric interactions between the atom occupying the 2-position in the bridge and the adjacent carbon atom in each cyclopentadienyl ring. Asymmetry in these angles is also notable in I (124.3 and 129.4° at C(1), 123.8 and 127.1° at C(6)), but the Se(2) · · · C(5) and Se(2) · · · C(10) contacts of 3.674 and 3.713 Å respectively lie outside the sum of the Van der Waals radii for Se and C (3.5 Å). An alternative explanation may lie in the interaction of the Ru and Se(2) atoms which are only 3.845 Å apart.

The molecular packing, Fig. 2, is unusual in that it involves an alternation, along the *a* axis, of regions containing the metallocene and triselena moieties. The only short intermolecular contacts (Table 5) are of the Se · · · Se type, for which the Van der Waals sum is 4.0 Å. The intermolecular contacts in I are comparable to those observed in elemental selenium [16]. I has a two-dimensional network of selenium atoms in the *bc* plane.

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