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The synthesis and crystal structure of 1,2,3-trithia[3]osmocenophane

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Abstract

The first bridged osmocene compound, 1,2,3-trithia[3]osmocenophane (I), has been prepared by the reaction of 1,1′-dilithioosmocene with elemental sulphur, and its crystal structure determined by X-ray diffraction methods. The S–S bond lengths are 2.039(9) and 2.055(9) Å and the S–S–S bond angle is 106.4(4)°. The S–C bond lengths are 1.760(12) and 1.752(11) Å with S–S–C bond angles of 103.1(5) and 103.5(5)°. The cyclopentadienyl rings are in an eclipsed conformation and are slightly inclined to each other, with a non-bonded S(1)–S(3) separation of 3.279 Å.

Introduction

Although a large number of [*n*]ferrocenophanes and fewer [*n*]ruthenocenophanes are known, involving a variety of organic and inorganic bridging units, as far as we are aware there has been no report of a compound in which the cyclopentadienyl rings of osmocene are linked together. [3]Ferro- and [3]ruthenocenophanes containing trichalcogen bridges have been prepared [1–5] and several have been structurally characterised by X-ray diffraction [4–7]. The greater inter-ring separation in osmocene (3.71 Å) in comparison with ruthenocene (3.68 Å) and ferrocene (3.32 Å) leads to interest in the effect on the bridge geometry in analogous osmocenophanes.

We now report the synthesis of the first example of an osmocenophane, namely 1,2,3-trithia[3]osmocenophane, which involves a bridge of three sulphur atoms linking the two cyclopentadienyl rings. The crystal and molecular structure of the compound is also reported and comparisons are drawn with the other structures featuring the osmocene moiety, namely, osmocene [8], decamethylosmocene [9]

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and several osmocenium salts [10–13] as well as with analogous ferro- and rutheno-cenophanes.

Experimental

General

All preparations were carried out by standard Schlenk techniques [14]. All solvents were freshly distilled, dried and degassed before use and all reactions were performed under purified nitrogen.

Elemental analysis was performed by C.H.N. Analysis, South Wigston, Leicester. ^1H NMR spectra were recorded on a Brüker AM250 FT spectrometer, operating at 250.13 MHz. The spectra were recorded as $CDCl_3$ solutions with the ^1H chemical shifts being quoted relative to Me_4Si as internal standard.

1,2,3-Trithia[3]osmocenophane

The synthesis was based on the approach used by Bishop *et al.* [1] for the formation of the analogous iron compound. A suspension of 1,1'-dilithioosmocene-bis(*N*,*N*,*N'*,*N'*-tetramethylethylenediamine) was prepared by stirring for 18 h a mixture of n-butyllithium (1.6 *M*, 2.81 ml, 4.5 mmol), osmocene (0.512 g, 1.6 mmol) and *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (0.68 ml, 4.5 mmol) in hexane (40 ml). The suspension was then cooled to −20°C and the supernatant liquid removed. Hexane (40 ml) and sulphur flowers (0.32 g, 10 mmol) were added and the mixture was refluxed for 7 h, then cooled and filtered to remove excess sulphur. Crystallisation from hot hexane produced pale yellow crystals (0.12 g, 20%; m.p. 188°C). Anal. Found: C, 29.15; H, 2.12. $C_{10}H_8OsS_3$ calc.: C, 28.99; H, 1.93%. ^1H NMR ($CDCl_3$) δ (ppm): 4.30 (2H, m), 4.94 (2H, m), 5.03 (2H, m), 5.13 (2H, m).

X-ray structure determination

Crystal data for $C_{10}H_8OsS_3$: M 414.57, triclinic, space group $P\bar{1}$, a 7.784(2), b 7.992(5), c 8.625(4) Å, α 103.67(4), β 90.56(3), γ 101.87(3)°, U 509.25 Å^3, $Z = 2$, D_c 2.704 g cm^{-3}, $F(000) = 384$, λ 0.71069 Å, μ(Mo-K_α) 130.82 cm^{-1}.

Data collection

Unit cell parameters and intensity data were obtained by previously detailed procedures [15] on a CAD4 diffractometer using graphite-monochromated Mo-K_α radiation and an ω–2θ scan mode. A total of 1347 unique reflections was collected ($3 \leq 2\theta \leq 54°$). The reflection intensities were corrected for absorption, using the azimuthal-scan method [16].

Solution and refinement of structure

The structure was solved by the application of routine heavy-atom methods (SHELX-84) [17], and refined by full-matrix least squares (SHELX-76) [18]. The carbon atoms were refined as forming a regular pentagon with C–C 1.395 Å and angle C–C–C 108°. Hydrogen atoms were positioned on their parent carbon atoms with C–H 0.96 Å.

The final residuals R and R_w were 0.045 and 0.052 respectively for the 61 variables and 1190 reflections for which $F_o > 5\sigma(F_o)$. Atomic scattering factors and

Table 1

Fractional atomic coordinates [a] ($\times 10^4$) for $C_{10}H_8OsS_3$

Atom	x	y	z
Os	2717(9)	6862(9)	3451(8)
S(1)	645(7)	9539(7)	1878(6)
S(2)	2848(7)	9551(6)	617(6)
S(3)	2797(7)	6969(7)	−511(5)
C(1)	1200(10)	8880(10)	3581(10)
C(2)	171(10)	7443(10)	4087(10)
C(3)	1045(10)	7264(10)	5473(10)
C(4)	2615(10)	8591(10)	5823(10)
C(5)	2711(10)	9590(10)	4654(10)
C(6)	3478(11)	6110(10)	1034(10)
C(7)	5012(11)	6737(11)	2085(10)
C(8)	4964(11)	5602(10)	3133(10)
C(9)	3400(11)	4272(10)	2730(10)
C(10)	2482(11)	4587(10)	1433(10)

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

anomalous scattering parameters were taken from refs. 19 and 20 respectively. All computations were made on a DEC VAX-11/750 computer. A full table of bond lengths and angles, and lists of thermal parameters and structure factors are available from the authors.

Results and discussion

The osmocenophane was obtained in 20% yield as pale yellow crystals. These crystals were air-stable, although they were found to decompose when subjected to column chromatography on Grade II alumina. The ^1H NMR spectrum of the compound is temperature dependent. At ambient temperature the spectrum consists of 4 multiplets, consistent with an ABCD pattern, but in dynamic NMR studies changes were observed which can be attributed to a bridge reversal process; this is discussed elsewhere [21]. For further characterisation of this novel bridged osmocene compound, an X-ray crystal structure was obtained.

Atomic parameters for the crystal structure are given in Table 1 and a view of the molecule illustrating the numbering scheme is shown in Fig. 1.

Bond distances and selected bond angles are noted in Tables 2 and 3 respectively. The C–C distances and the C–C–C angles were set at the idealised values of 1.395 Å and 108° respectively for ferrocenyl and ruthenocenyl compounds [4–6,22–24]. Mean bond distances from Os to C are 2.176(11) Å and these compare with 2.19(1) Å in osmocene [8] and 2.18(1) Å in decamethylosmocene [9].

The two S–S bond lengths show a slight asymmetry (2.039(9) and 2.055(9) Å) but are similar to those found in the analogous tri-sulphur bridged ferrocenophane (2.048(4) and 2.050(4) Å) [6]. The S–C bond lengths (1.752(11) and 1.760(12) Å) are again similar though slightly larger than those in the ferrocenophane (1.749(9) and 1.746(10) Å). The S–S–S angle of 106.4(4)° found in the osmocenophane is, as expected, greater than the angle (103.9(2)°) in the ferrocenophane, due to the increased inter-ring separation in the former compound. This trait of increased bridgehead angle with increasing inter-ring distance is also prevalent in the analogous triselenium-[3]ferrocenophane (100.7°) [7] and -[3]ruthenocenophane

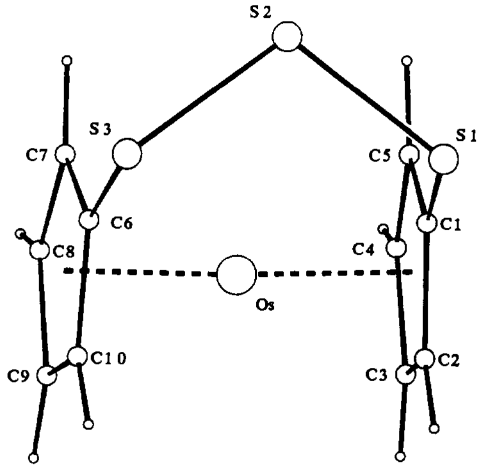

Fig. 1. A view of the X-ray crystal structure of $C_{10}H_8OsS_3$ showing the numbering scheme adopted.

Table 2

Bond distances (Å) for $C_{10}H_8OsS_3$ [a]

S(1)-S(2)	2.039(9)	C(4)-Os	2.194(10)
S(2)-S(3)	2.055(9)	C(5)-Os	2.182(10)
C(1)-S(1)	1.752(11)	C(6)-Os	2.153(11)
C(6)-S(3)	1.760(12)	C(7)-Os	2.156(11)
C(1)-Os	2.169(11)	C(8)-Os	2.181(11)
C(2)-Os	2.173(11)	C(9)-Os	2.192(11)
C(3)-Os	2.188(11)	C(10)-Os	2.175(11)

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

Table 3

Selected bond angles (deg) [a] for $C_{10}H_8OsS_3$

S(1)-S(2)-S(3)	106.4(4)	C(7)-C(6)-S(3)	129.2(4)
C(1)-S(1)-S(2)	103.5(5)	C(10)-C(6)-S(3)	122.8(4)
C(6)-S(3)-S(2)	103.1(5)	S(1)-C(1)-Os	121.6(6)
C(2)-C(1)-S(1)	123.6(4)	S(3)-C(6)-Os	122.7(6)
C(5)-C(1)-S(1)	128.4(4)		
C(1)-C(2)-Os	70.8(3)	C(5)-C(1)-Os	71.5(3)
C(2)-C(3)-Os	70.4(3)	C(5)-C(4)-Os	70.6(3)
C(3)-C(4)-Os	70.9(3)	C(4)-C(3)-Os	71.3(3)
C(4)-C(5)-Os	71.5(3)	C(3)-C(2)-Os	71.6(3)
C(1)-C(5)-Os	70.5(3)	C(2)-C(1)-Os	71.1(3)
C(6)-Os-C(1)	108.2(4)	C(6)-Os-C(7)	38.5(2)
C(6)-Os-C(2)	124.3(4)	C(6)-Os-C(8)	64.0(4)
C(6)-Os-C(3)	160.1(3)	C(6)-Os-C(9)	63.8(4)
C(6)-Os-C(4)	157.5(3)	C(6)-Os-C(10)	38.3(2)
C(6)-Os-C(5)	122.6(4)		
C(1)-Os-C(2)	38.2(2)	C(4)-Os-C(2)	63.5(3)
C(1)-Os-C(3)	63.6(3)	C(4)-Os-C(3)	37.8(1)
C(1)-Os-C(4)	63.5(3)	C(5)-Os-C(2)	63.7(3)
C(1)-Os-C(5)	38.1(1)	C(5)-Os-C(3)	63.4(3)
C(3)-Os-C(2)	38.0(1)	C(5)-Os-C(4)	37.9(1)

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

Table 4

Equations of selected least-squares mean planes

Cyclopentadienyl ring C(1)–C(5)
$-5.0597\,X + 4.8090\,Y + 3.9901\,Z = 5.1236$

Deviations from plane (Å)	C(1)	0.0190	C(2)	−0.0174
	C(3)	0.0097	C(4)	0.0018
	C(5)	−0.0130	S(1)	−0.1171
	S(2)	−1.7270	S(3)	−3.3955
	Os	−1.8192	C(6)	−3.5095
	C(7)	−3.5507	C(8)	−3.6733
	C(9)	−3.6847	C(10)	−3.5722

Cyclopentadienyl ring C(6)–C(10)
$-4.9093\,X + 4.3534\,Y + 4.5989\,Z = 1.4620$

Deviations from plane (Å)	C(6)	−0.0081	C(7)	0.0071
	C(8)	−0.0032	C(9)	−0.0017
	C(10)	0.0059	S(3)	−0.0406
	S(2)	1.5798	S(1)	3.2336
	Os	1.7807	C(1)	3.5137
	C(2)	3.5566	C(3)	3.6886
	C(4)	3.6671	C(5)	3.5363

(102.5°) [5] species. The effect of this angle on the ease of bridge reversal is discussed elsewhere [21]. It is thought that the wider bridgehead angle represents a reduction in bond angle strain [5] and this is further illustrated by the unequal S–S–C angles in the trisulphur-iron derivative (102.3(3) and 103.3(4)°) as compared with the virtually identical angles (103.5(5) and 103.1(5)°) found in the osmocenophane. Differences in the osmocenyl exocyclic C–C–S bond angles (123.6(4) and 128.4(4)° at C(1) and 122.8(4) and 129.2(4)° at C(6)) are observed. This asymmetry is a structural feature common to [3]metallocenophanes of this

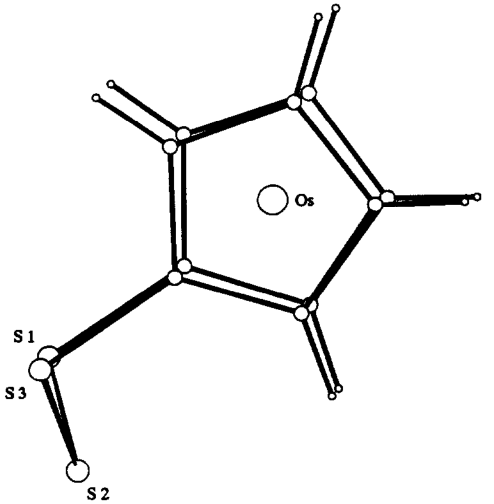

Fig. 2. A view of the molecule illustrating the eclipsed nature of the cyclopentadienyl rings.

type and has been attributed to steric interactions between the atom occupying the 2-position in the bridge and the adjacent carbon atom in each ring [25].

Equations for selected least-squares mean planes are given in Table 4. The cyclopentadienyl rings are planar within limits of error, and adopt an eclipsed configuration, as is clearly shown in Fig. 2. The rings are not precisely parallel, the angle between the normals to the ring planes being 4.74°, in comparison with an angle of 2.85° in the analogous ferrocenophane.

The two S atoms are displaced from the mean planes of the rings to which they are attached by 0.12 Å for S(1) and 0.04 Å for S(3), giving rise to a non-bonded S · · · S separation of 3.279 Å. However, the displacements are unexpectedly all in one direction and this illustrates the asymmetry or skewness of the structure, which is further illustrated by the osmium atom lying 1.82 Å from the C(1)–C(5) ring plane and 1.78 Å from the C(6)–C(10) ring plane.

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