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Ferrocenium μ -Bromo-bis[dibromodimethylstannate(IV)]

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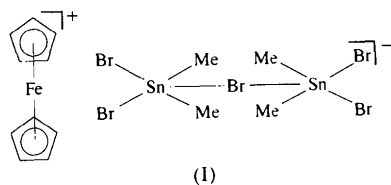
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Abstract

The ferrocenium cation of the title compound, [Fe(C₅H₅)₂][Sn₂Br₅(CH₃)₄], has parallel cyclopentadienyl rings with an eclipsed conformation. The Sn atom of the anion is in a distorted square-pyramidal coordination. Alternatively, it can be described as having a distorted octahedral coordination, forming infinite chains of two edge-shared octahedra parallel to the *b* axis.

Comment

Although the structures of several ferrocenium salts with halogeno-metal anions such as tetrachloroferrate (Paulus & Schafer, 1978) and tetrachloroantimonate (Yamin *et al.*, 1996) have been reported, no structural information for ferrocenium with tin counteranions was found in the literature, except for the suggested molecular formula of [(C₅H₅)₂Fe]₂(SnCl₃)(SnCl₅)(SnCl₄)·H₂O (Watanabe *et al.*, 1986) for the oxidized product of ferrocene with SnCl₄ in hexane. Furthermore, the ferrocenium–tin tetrahalide salts were said to be highly hygroscopic. In contrast, we were able to obtain good quality crystals of the title compound, (I), from the reaction of ferrocene with dimethyltin dibromide.



The asymmetric unit contains half a ferrocenium cation and half a μ -bromo-bis[dibromodimethylstannate(IV)] anion. The other halves are generated by mirror symmetry, with C3, C6 and Br3 lying on the mirror plane (Fig. 1). The cyclopentadiene rings in the

ferrocenium cation are nearly parallel, having a dihedral angle of only 2.0(8)° between them, and they are completely eclipsed. The C—C and Fe—C bond distances, and the Fe—ring centroid distances [1.709(6) and 1.693(6) Å] in the ferrocenium moiety agree with reported mean values (Orpen *et al.*, 1989). The Sn atom may be described as possessing a distorted trigonal-

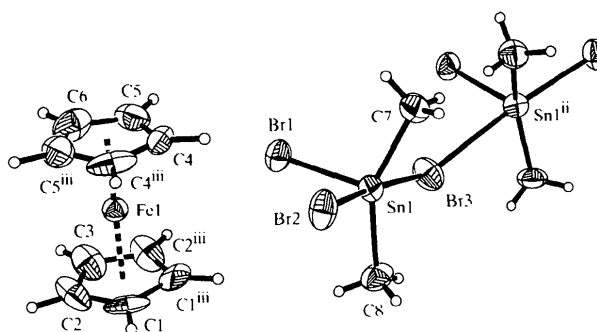


Fig. 1. The structure of title compound showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms have small arbitrary radii for clarity. [Symmetry codes: (ii) $x, \frac{1}{2} - y, z$; (iii) $x, \frac{3}{2} - y, z$.]

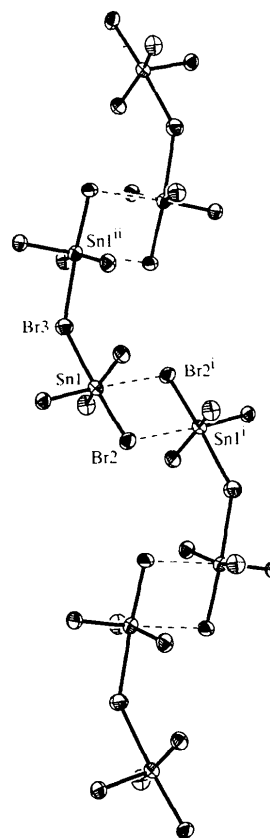


Fig. 2. Part of the infinite chain of octahedra running parallel to the *b* axis. The octahedra share both vertices (at Br3) and edges (Br2–Br2') [symmetry codes: (i) $1 - x, 1 - y, -z$; (ii) $x, \frac{1}{2} - y, z$].

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bipyramidal coordination, the distortions from ideal angles being confined to the equatorial plane. The calculated τ value (Addison *et al.*, 1994) is 0.44. The Br3 atom on the mirror plane acts as a bridge to the other half of the anion. However, the Sn—Br2ⁱ distance of 3.573 (2) Å is appreciably less than the sum of the corresponding van der Waals radii of 4.05 Å [symmetry code: (i) 1 - x, 1 - y, -z]. If this bonding is considered to be significant, then the coordination around the Sn atom may be alternatively explained as distorted octahedral with the C7, C8, Br1 and Br2ⁱ atoms occupying the equatorial positions, and the Br2 and Br3 atoms in axial positions. Here, the Br3 atom links two Br2—Br2ⁱ edge-shared octahedra to form infinite chains parallel to the *b* axis. The Sn—Br and Sn—C distances agree with reported values (Shcherbakov *et al.*, 1987).

Experimental

Equimolar concentrations of ferrocene and dimethyltin dibromide in benzene were mixed in a flask. The solution was left to evaporate. After about two weeks, blue-black crystals were obtained. These crystals were washed with hexane and dried.

Crystal data

[Fe(C₅H₅)₂][Sn₂Br₅(CH₃)₄]

$M_r = 883.10$

Orthorhombic

Pnma

$a = 11.999 (2) \text{ \AA}$

$b = 15.450 (2) \text{ \AA}$

$c = 13.197 (2) \text{ \AA}$

$V = 2446.5 (6) \text{ \AA}^3$

$Z = 4$

$D_x = 2.398 \text{ Mg m}^{-3}$

D_m not measured

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 42 reflections

$\theta = 5.48\text{--}12.49^\circ$

$\mu = 10.772 \text{ mm}^{-1}$

$T = 293 (2) \text{ K}$

Rectangular plate

$0.26 \times 0.18 \times 0.10 \text{ mm}$

Blue-black

Data collection

Siemens P4 diffractometer

$\theta/2\theta$ scans

Absorption correction:

empirical via ψ scans

(Siemens, 1994)

$T_{\min} = 0.161$, $T_{\max} = 0.341$

3637 measured reflections

2881 independent reflections

816 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.068$

$\theta_{\max} = 27.50^\circ$

$h = -1 \rightarrow 15$

$k = -20 \rightarrow 1$

$l = -1 \rightarrow 17$

3 standard reflections

every 97 reflections

intensity decay: <3%

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.043$

$wR(F^2) = 0.107$

$S = 0.704$

2880 reflections

106 parameters

H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0274P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.77 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.85 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Sn1	0.52149 (7)	0.43449 (5)	0.16115 (6)	0.0646 (3)
Br1	0.50985 (11)	0.46309 (7)	0.35033 (10)	0.0802 (4)
Br2	0.45824 (13)	0.59323 (7)	0.10697 (10)	0.0886 (5)
Br3	0.6029 (2)	1/4	0.2028 (2)	0.0991 (8)
Fe1	0.4978 (2)	3/4	0.4119 (2)	0.0526 (6)
C1	0.6342 (9)	0.7972 (9)	0.3336 (10)	0.099 (6)
C2	0.6431 (11)	0.8223 (9)	0.4349 (12)	0.100 (6)
C3	0.6462 (15)	3/4	0.4948 (18)	0.099 (8)
C4	0.3545 (8)	0.7047 (9)	0.3464 (9)	0.094 (6)
C5	0.3569 (10)	0.6807 (9)	0.4447 (12)	0.091 (5)
C6	0.3616 (17)	3/4	0.5051 (15)	0.108 (8)
C7	0.3686 (8)	0.3739 (6)	0.1234 (8)	0.083 (4)
C8	0.6901 (8)	0.4531 (7)	0.1286 (9)	0.087 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Sn1—Br1	2.539 (2)	Sn1—Br3	3.063 (1)
Sn1—Br2	2.6651 (14)	Sn1—C8	2.089 (10)
Sn1—Br2 ⁱ	3.573 (2)	Sn1—C7	2.119 (9)
Br1—Sn1—Br2	95.05 (5)	C7—Sn1—Br2	95.6 (3)
Br1—Sn1—Br2 ⁱ	176.78 (4)	C7—Sn1—Br2 ⁱ	76.9 (3)
Br2—Sn1—Br2 ⁱ	82.18 (4)	C8—Sn1—Br2	95.4 (3)
Br3—Sn1—Br2 ⁱ	92.55 (6)	C8—Sn1—Br2 ⁱ	75.3 (3)
Br1—Sn1—Br3	90.17 (6)	C7—Sn1—Br3	84.7 (3)
Br2—Sn1—Br3	174.51 (7)	C8—Sn1—Br3	81.7 (3)
C7—Sn1—Br1	105.1 (3)	C7—Sn1—C8	148.3 (4)
C8—Sn1—Br1	103.4 (3)	Sn1—Br3—Sn1 ⁱⁱ	137.07 (7)

Symmetry codes: (i) 1 - x, 1 - y, -z; (ii) $x, \frac{1}{2} - y, z$.

The title structure was solved by direct methods and refined by full-matrix least-squares techniques. All H atoms were geometrically fixed and allowed to ride on their parent atom. Although the displacement parameters of some atoms in the cyclopentadienyl rings show possible signs of incipient disorder, no viable disorder model could be developed.

Data collection: XSCANS (Siemens, 1994). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: SHELXL93, PLATON (Spek, 1990) and PARST (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1212). Services for accessing these data are described at the back of the journal.

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Bis[2,2'-iminodipyridinium(1+)] Bis[μ -4-hydroxy-2,6-pyridinedicarboxylato(3-)]bis[μ -aquadibutyltin(IV)] Dihydrate†

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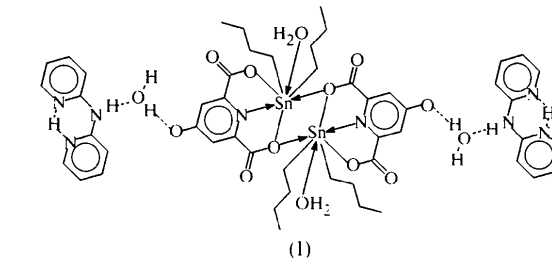
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Abstract

The water-coordinated Sn atom in the centrosymmetric title compound, (C₁₀H₁₀N₃)₂[Sn₂(C₇H₂NO₅)₂·(C₄H₉)₄(H₂O)₂].2H₂O, is seven-coordinate in a *trans*-C₂SnNO₄ pentagonal-bipyramidal geometry [C—Sn—C 156.6(1)°]. The dianion is linked to two planar 2,2'-iminodipyridinium(1+) cations through the lattice water molecules *via* the amino bridges [O_{water}···N_{amino} 2.810(5), O_{water}···O_{hydroxy} 2.633(4) and O_{water}···O_{carbonyl} 2.927(5) Å]. A weaker water–water interaction connects the ion pair into a linear helical chain.

Comment

Dibutyltin oxide condenses with dicyclohexylammonium 2,6-pyridinedicarboxylate to yield bis(dicyclohexylammonium) bis[dibutyl(2,6-pyridinedicarboxylato)stannate] (Ng *et al.*, 1997), but with methylphenylammonium 2,6-pyridinedicarboxylate to give bis[aquadibutyl(2,6-pyridinedicarboxylato)tin] *N*-methylaniline solvate (Ng, 1998*b*). In the *N*-methylaniline solvate,



Di-2-pyridylamine exists as a hydrogen-bonded dimer in two modifications: a low-melting polymorph and a high-melting polymorph. The pyridyl N atom is protonated in preference to the amino N atom, since

† Alternative name: bis[2,2'-iminodipyridinium(1+)] diaqua-1 κ O,2 κ O-tetrabutyl-1 κ^2 C¹,2 κ^2 C¹-bis[μ -4-hydroxy-2,6-pyridinedicarboxylato(3-)]-1 κ^3 O²,N,O⁶:2 κ O⁶:2 κ^3 O²,N,O⁶:1 κ O⁶-ditin(IV) dihydrate.