Experimental

The metal-free hemiporphyrazine ligand (hpH2) was synthesized according to a published procedure (Dirk & Marks, 1984). *trans*-Dichloro(hemiporphyrazinato)tin(IV) was synthesized by refluxing hpH_2 (1.0 g, 2.3 mmol) and $SnCl_4{\cdot}5H_2O$ (1.0 g, 2.9 mmol) in 10 ml of 1-chloronaphthalene for 45 min. The hot reaction vessel was then suspended in 463 K silicon oil in a dewar and slowly cooled to room temperature. Crystals suitable for X-ray diffraction formed over the course of several hours.

Crystal data

$[SnCl_2(C_{26}H_{14}N_8)]$
$M_r = 628.04$
Monoclinic
$P2_1/n$
$a = 7.6544\,(12)$ Å
$b = 15.351\,(3)$ Å
$c = 10.287\,(2)$ Å
$\beta = 106.544\,(8)°$
$V = 1158.69\,(2)$ Å^3
$Z = 2$
$D_x = 1.800$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4116 reflections
$\theta = 0.00$–$28.29°$
$\mu = 1.37$ mm^{-1}
$T = 153\,(2)$ K
Needle
$0.27 \times 0.04 \times 0.04$ mm
Dark green

Data collection

Siemens SMART diffractometer
0.3° ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min} = 0.73$, $T_{\max} = 0.96$
8149 measured reflections

2842 independent reflections
2011 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.053$
$\theta_{\max} = 28.29°$
$h = -10 \rightarrow 10$
$k = -20 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.120$
$S = 0.999$
2842 reflections
169 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0689P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.10$ e Å^{-3}
$\Delta\rho_{\min} = -2.06$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Sn—N3 (isoindole)	2.041 (3)	Sn—Cl	2.4214 (11)
Sn—N1 (pyridine)	2.213 (4)		
N3—Sn—N1	90.27 (13)	N1^i—Sn—Cl	88.86 (10)
N3^i—Sn—N1	89.73 (13)	N3—Sn—Cl	90.82 (11)
N1—Sn—Cl	91.13 (10)	N3^i—Sn—Cl	89.17 (11)
N1—Sn—Cl^i	88.87 (10)	N3—Sn—Cl^i	89.18 (11)

Symmetry code: (i) $-x, -y, -z$.

Crystals were handled under a light hydrocarbon oil. The datum crystal was affixed with a small amount of silicone vacuum grease to a thin glass fiber on a tapered copper mounting pin and mounted on the goniometer head. An arbitrary hemisphere of space was collected at 30 s per 0.3° ω scan. Coverage to 0.75 Å was 92%, and 99% to 0.80 Å. No decay was observed in 50 frames remeasured on completion of the data collection. The largest features in the final difference map were 1.10 e Å^{-3} at 0.87 Å from Sn and -2.06 e Å^{-3} at 0.88 Å from Sn.

Data collection: *SMART* (Siemens, 1996). Cell refinement: *SAINT* (Siemens, 1996). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BK1399). Services for accessing these data are described at the back of the journal.

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1,1′-Diiodo-3,3′-bis(trimethylsilyl)ferrocene

DANIEL A. FOUCHER,[a] ALAN J. LOUGH[b] AND PETER PARK[b]

[a]*Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1, and* [b]*Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 3H6. E-mail: alough@.chem.utoronto.ca*

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Abstract

In the structure of the title compound, $[Fe(C_8H_{12}ISi)_2]$, the cyclopentadienyl rings are fully eclipsed. The trimethylsilyl groups are staggered by 141.0 (4)° and the iodo groups by 69.6 (3)°.

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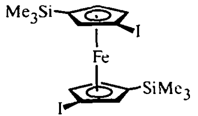
Comment

Poly(1,1′-ferrocenylenes), which are polymers comprised of a backbone of only ferrocene units, are particularly attractive synthetic targets for materials which could possess interesting and unusual properties, such as mixed valency, ferromagnetic and optical states (Brown *et al.*, 1975; Seki *et al.*, 1991; Zhanru *et al.*, 1996). In order to prepare metallo-polymers of this type, ferrocenes with functionalized cyclopentadienyl rings bearing both reactive and solubilizing groups are crucial for successful high-molecular-weight step-growth polymerization (Sanechika *et al.*, 1981; Hirao *et al.*, 1996). As part of our overall effort to prepare ferrocenes of this type, a symmetrically substituted bis(trimethylsilyl)ferrocene was targeted as a synthon to soluble poly(1,1′-ferrocenylenes). The monomer, 1,1′-diiodo-3,3′-bis(trimethylsilyl)ferrocene, (I), was synthesized from the reaction of 1,1′-bis(tri-*n*-butylstannyl)-3,3′-bis(trimethylsilyl)ferrocene and iodine. A previous attempt (Brown *et al.*, 1992) to prepare the starting material was unsuccessful.



(I)

In the structure of (I) (Fig. 1), the two Cp rings are essentially eclipsed. The trimethylsilyl groups are staggered by 141.0 (4)° (as defined by the dihedral angle Si1—*Cp*1—*Cp*2—Si2, where *Cp*1 is the centroid of the C6–C10 ring and *Cp*2 is the centroid of the C1–C5 ring) and the iodo groups by 69.6 (3)° (as defined by the dihedral angle I1—*Cp*1—*Cp*2—I2). This conformation of the cyclopentadienyl rings and the positions of the substituent groups allow the best possible relief from steric interaction of the bulky groups. For comparison, the absence of additional groups on the cyclopentadienyl rings allows the trimethylsilyl substituents of 1,1′-bis(trimethylsilyl)ferrocene to be ideally staggered and *trans* to each other (Foucher *et al.*, 1995). The trimethylsilyl and iodo groups lie slightly out of the plane of the cyclopentadienyl ring C atoms. Si1 and Si2 are bent away from the Fe center by 0.029 (5) and −0.079 (5) Å, respectively, while I1 and I2 deviate from the Fe center by 0.090 (6) and 0.121 (6) Å, respectively. The observed deviation of the substituents, from the cyclopentadienyl rings away from the Fe atom, is again probably due to the steric interaction of the bulky substituents. Also present is a slight deviation from 180° of the *Cp*1—Fe1—*Cp*2 angle [178.7 (3)°], with a displacement of 0.018 (2)° of Fe1 from the midpoint of the ring centroids and an accompanying tilt angle (which is the angle between the least-squares planes of the cyclopentadienyl rings) of 0.7 (3)°. The C—I bond lengths of 2.073 (4) and 2.067 (3) Å are comparable to those found in other iodobiferrocene compounds (Dong *et al.*, 1995).

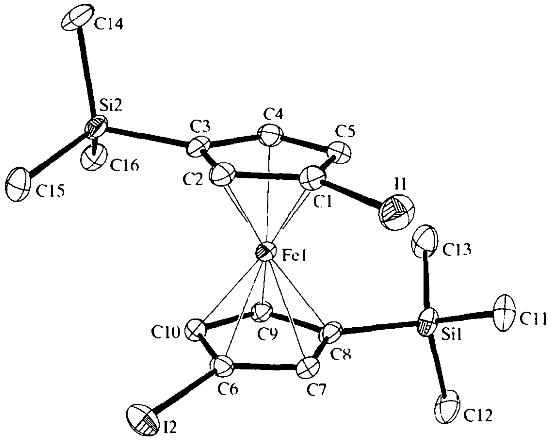


Fig. 1. View of the title molecule, showing the atom-labeling scheme. Displacement ellipsoids are shown at the 30% probability level.

Experimental

The title compound was prepared using a variation of the halogen/organotin exchange reaction previously reported by Butler *et al.* (1993). Iodine (49.9 g, 0.196 mol) was added to a stirred solution of 1,1′-bis(tri-*n*-butylstannyl)-3,3′-bis(trimethylsilyl)ferrocene (80.9 g, 0.089 mol) in CH_2Cl_2 (450 ml) at 273 K. This gave a dark green–brown solution which was allowed to warm-up to ambient temperature and was then stirred for 18 h. The resulting dark red–brown solution was washed with 1 *M* sodium thiosulfate (2 × 200 ml aliquots). The organic phase was then filtered through neutral alumina and the solvent removed to yield a dark amber oil. The oil was redissolved in methanol (300 ml) containing potassium fluoride (20 g, 0.344 mol). After stirring for 10 min, a thick bright-yellow slurry formed. The slurry was filtered through neutral alumina and the solvent removed to leave an orange residue. This residue was extracted with diethyl ether (300 ml) and the resulting etheric solution was washed three times with water (200 ml). The organic phase was then dried, and purified by column chromatography using hexanes as the eluent. After removing the solvent, dark amber crystals of (I) (15.4 g, 29.7% yield) formed from the resulting oil. ^1H NMR (p.p.m.): 4.53 (*m*), 3.93 (*m*), 3.89 (*m*), 0.27 (*s*); ^{13}C NMR (p.p.m.): 78.2, 76.0, 42.6, −0.20; MS (EI, 70 eV) *m/z* (%): 582 (100, M^+), 440 (26, $M - CH_3$, I); high resolution MS: $C_{16}H_{24}FeI_2Si_2$ calculated 581.8856, measured 581.8837; elemental analysis (%) found (calculated): C 33.23 (33.01), H 4.03 (4.16).

Crystal data

[Fe($C_8H_{12}ISi$)$_2$]
M_r = 582.18
Monoclinic
$P2_1/n$
a = 12.0436 (9) Å
b = 9.1870 (5) Å
c = 18.7995 (10) Å
β = 93.128 (8)°
V = 2077.0 (2) Å^3
Z = 4
D_x = 1.862 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 47 reflections
θ = 5.25–22.95°
μ = 3.807 mm^{-1}
T = 173 (2) K
Needle
0.52 × 0.38 × 0.27 mm
Orange–red

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: semi-empirical *via* ψ scan (Sheldrick, 1995)
$T_{\min} = 0.117$, $T_{\max} = 0.358$
6305 measured reflections
6047 independent reflections
4398 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.032$
$\theta_{\max} = 30.01°$
$h = -15 \rightarrow 16$
$k = -9 \rightarrow 12$
$l = -26 \rightarrow 26$
3 standard reflections every 97 reflections intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.098$
$S = 0.922$
6047 reflections
197 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.085$ e Å^{-3}
$\Delta\rho_{\min} = -1.159$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.00113 (15)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

I1—C1	2.074 (4)	Si1—C8	1.849 (4)
I2—C6	2.067 (3)	Si2—C3	1.852 (4)
C5—C1—I1	125.3 (3)	C10—C6—I2	125.2 (3)
C2—C1—I1	125.5 (3)	Fe1—C6—I2	129.2 (2)
C2—C3—Si2	127.0 (3)	C9—C8—Si1	126.8 (3)
C4—C3—Si2	126.6 (3)	C7—C8—Si1	127.5 (3)
Si2—C3—Fe1	129.5 (2)	Si1—C8—Fe1	127.8 (2)
C7—C6—I2	125.7 (2)		

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1995). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1467). Services for accessing these data are described at the back of the journal.

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Hexaaquametal(II) 4-styrenesulfonates of manganese, cobalt and nickel

Melvin A. Leonard,[a] Philip J. Squattrito[a] and Surendra N. Dubey[b]

[a]*Department of Chemistry, Central Michigan University, Mount Pleasant, Michigan 48859, USA, and* [b]*Department of Chemistry, Kurukshetra University, Kurukshetra 136 119, Haryana, India. E-mail: philip.squattrito@cmich.edu*

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Abstract

The title compounds form an isomorphous series of the general formula $[M(H_2O)_6](C_8H_7SO_3)_2$, where M = Mn {hexaaquamanganese(II) bis(4-styrenesulfonate), $[Mn(H_2O)_6](C_8H_7SO_3)_2$}, Co {hexaaquacobalt(II) bis(4-styrenesulfonate), $[Co(H_2O)_6](C_8H_7SO_3)_2$} or Ni {hexaaquanickel(II) bis(4-styrenesulfonate), $[Ni(H_2O)_6](C_8H_7SO_3)_2$}. The three compounds share a structure built of alternating layers of hexaaquametal(II) cations and 4-styrenesulfonate anions. The coordination environments of the metal cations are octahedral, with only minor deviations from ideal geometries [Mn—O 2.126 (3)–2.176 (5) Å, O—Mn—O 84.6 (1)–89.9 (2)°; Co—O 2.052 (2)–2.087 (4) Å, O—Co—O 86.4 (1)–89.5 (1)°; Ni—O 2.021 (3)–2.041 (5) Å, O—Ni—O 87.8 (2)–89.6 (2)°]. The 4-styrenesulfonate layers contain alternating rows of anions, with the sulfonate groups directed towards opposite faces of the layer. The layers are held together by a two-dimensional array of O—H···O hydrogen bonds between the coordinated water molecules and sulfonate O atoms [O···O 2.717 (6)–2.816 (5) Å]. Similarities with the structures of other divalent metal arenesulfonate salts are described.

Comment

Previous studies have shown that the first-row transition metal cations tend to crystallize as hexaaqua complexes