

Tetraphenylphosphonium tetrakis(trimethylsilanolato)ferrate(III)

Michael T. Hay^{a*} and Hemant P. Yennawar^b

^aPenn State Beaver, 100 University Drive, Monaca, PA 15061, USA, and ^bThe Pennsylvania State University, Dept. Biochemistry and Molecular Biology, University Park, PA 16802, USA. *Correspondence e-mail: mth7@psu.edu

Received 18 December 2017

Accepted 20 December 2017

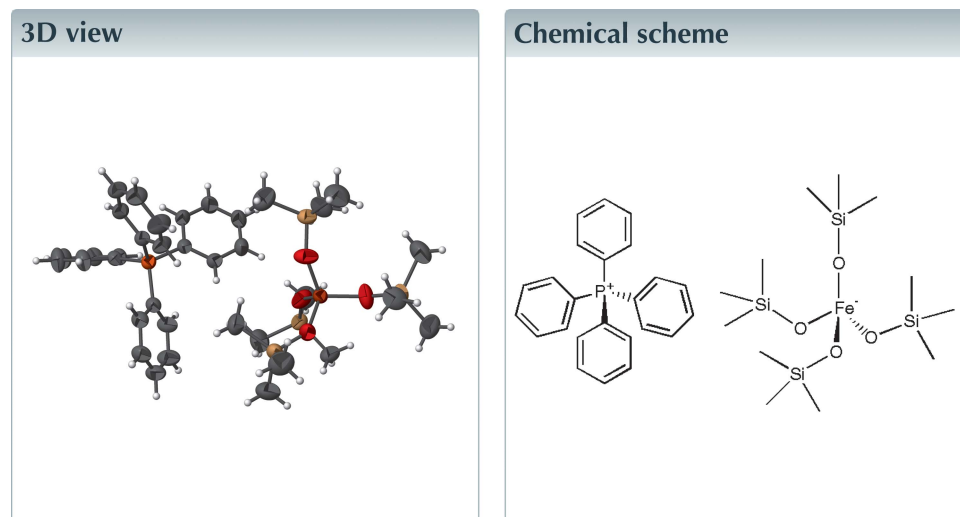
Edited by J. Simpson, University of Otago, New Zealand

Keywords: crystal structure; iron (III) complex; phosphonium salt.

CCDC reference: 1812775

Structural data: full structural data are available from iucrdata.iucr.org

The structure of tetraphenylphosphonium tetrakis(trimethylsilanolato)ferrate(III), $[(C_6H_5)_4P][Fe(OSi(CH_3)_3)_4]$, has tetragonal ($I\bar{4}$) symmetry, and was refined as an inversion twin. It is an ionic compound consisting of a tetraphenylphosphonium cation and a tetrakis(trimethylsilanolato)ferrate(III) anion. The crystal structure comprises the two ionic species each centered on a $\bar{4}$ symmetry element and contributing a fourth of its structure to the asymmetric unit. Each is surrounded by counter-ions on all sides. The cation contains a central phosphorous atom bound to four phenyl groups in a tetrahedral arrangement, while the anion contains a central iron(III) atom tetrahedrally coordinated by four trimethylsilanolato ligands.



Structure description

Previously, Hay *et al.* (2012) reported on the structural characterization of tetrabutylammonium tetrakis(trimethylsilanolato)ferrate(III) in order to make structural comparison with other tetrabutylammonium iron(III)-containing silsesquioxane compounds (Hay & Geib, 2007; Hay *et al.*, 2003, 2009). As we continue our work in the area of iron(III) silsesquioxane compounds, we have found that it would be useful to report the structural data of the analogous tetraphenylphosphonium iron(III) silanolate salt – the title compound.

The title compound contains a tetraphenylphosphonium cation and a tetrakis(trimethylsilanolato)ferrate(III) anion (Fig. 1). Each ionic species is centered on a $\bar{4}$ symmetry element and contributes a fourth of its structure to the asymmetric unit. The tetraphenylphosphonium cation, $(C_6H_5)_4P^{1+}$, consists of a tetrahedrally surrounded phosphorous atom, with P–C bond lengths that are all 1.789 (3) Å and with C–P–C bond angles in the range 107.1 (2)–110.69 (9)°. The complex anion, $[Fe(OSi(CH_3)_3)_4]^-$, contains a four-coordinate iron(III) atom with a tetrahedral arrangement of four tri-

Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
C6–H6···O1 ⁱ	0.94	2.47	3.359 (4)	158

Symmetry code: (i) $-y + 1, x, -z + 1$.

methylsilanolate ligands coordinating to it. The O–Fe–O bond angles are in the range 108.84 (9)–110.8 (2)°, while the Fe–O bond lengths are all 1.846 (2) Å.

The crystal structure comprises the two ionic species, each of which is surrounded by four counter-ions (Fig. 2). A C–H···O hydrogen bond stabilizes the lattice (Table 1). The phenyl rings of the tetraphenylphosphonium ions are not sufficiently close to their symmetry-related neighbors to be involved in π – π -type interactions.

A survey of the database (CSD; Groom *et al.*, 2016) returned two similar compounds, both with the tetrakis(trimethylsinalolato)ferrate(III) anion but with different cations. The first contained the tetramethylstibonium cation (CH₃)₄Sb⁺ (Schmidbauer, 1964) that crystallizes in an orthorhombic (*Pmnm*) space group. The second compound crystallizes in a triclinic (*P* $\bar{1}$) space group with a tetrabutylammonium cation [(C₄H₉)₄N⁺; Hay *et al.*, 2012). The Fe–O bond lengths in the second ferrate are slightly longer than in the title compound and range from 1.8515 (14)–1.8608 (13) Å, while the O–Fe–O bond angles span a wider range from 105.17 (6)–112.58 (6)° when compared to the title compound.

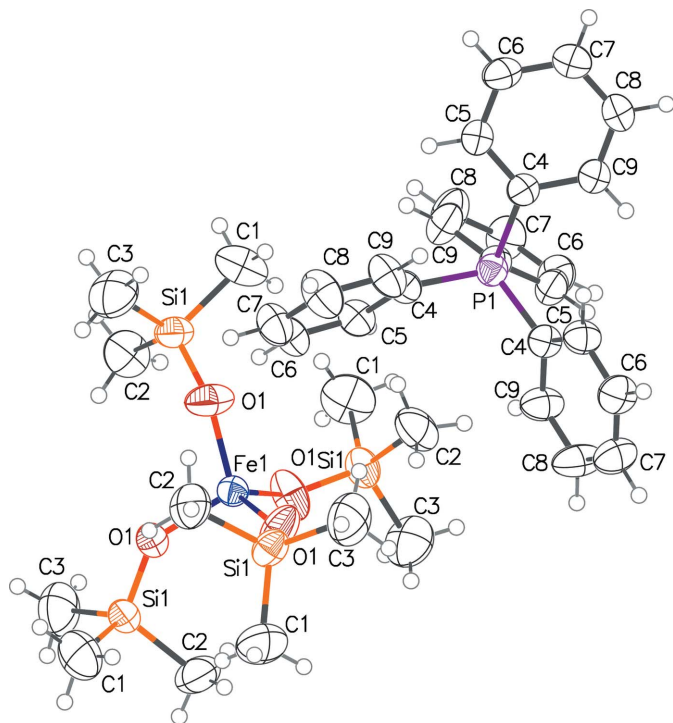


Figure 1
The molecular entities in the title salt showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

Table 2
Experimental details.

Crystal data	
Chemical formula	(C ₂₄ H ₂₀ P)[Fe(C ₃ H ₉ OSi) ₄]
<i>M_r</i>	751.98
Crystal system, space group	Tetragonal, <i>I</i> $\bar{4}$
Temperature (K)	223
<i>a</i> , <i>c</i> (Å)	12.589 (7), 13.689 (7)
<i>V</i> (Å ³)	2169 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.53
Crystal size (mm)	0.29 × 0.2 × 0.18
Data collection	
Diffractometer	Bruker CCD area detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Bruker, 2001)
<i>T_{min}</i> , <i>T_{max}</i>	0.600, 0.9
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	9779, 2712, 2258
<i>R_{int}</i>	0.050
(sin θ/λ) _{max} (Å ⁻¹)	0.676
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.036, 0.078, 0.92
No. of reflections	2712
No. of parameters	108
H-atom treatment	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.23, -0.23
Absolute structure	Refined as an inversion twin
Absolute structure parameter	0.02 (2)

Computer programs: *SMART* and *SAINT* (Bruker, 2001), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

A yellow solution of [(C₆H₅)₄P][FeCl₄] (0.372 mmol, 0.200 g, Jana *et al.*, 2009) in dichloromethane (2–3 ml) was treated with

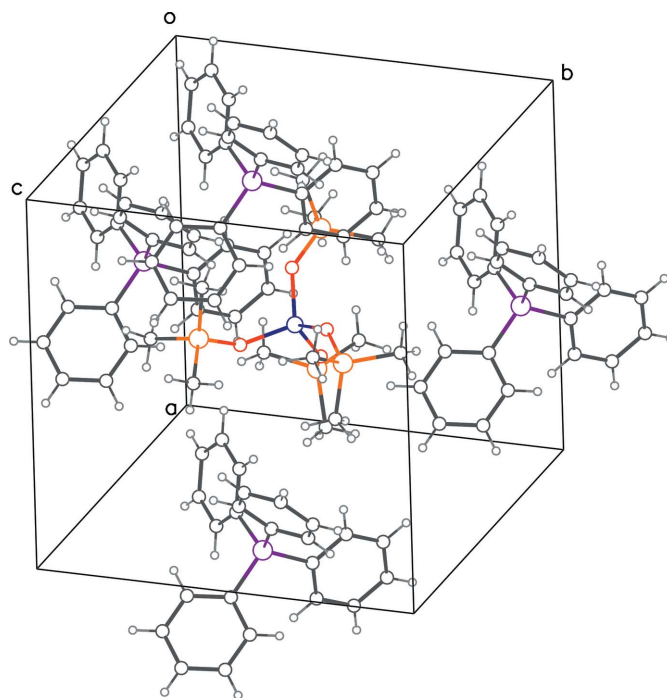


Figure 2
A packing diagram showing the ferrate anion surrounded by four phosphonium cations.

four equivalents of sodium trimethylsilanate (1.49 mmol, 0.167 g) dissolved in dichloromethane (2–3 ml). Immediately, the yellow color of the solution began to dissipate, as a white precipitate formed. The reaction mixture was stirred for 2–3 h before the precipitate was removed by filtration through celite, giving a clear colorless filtrate. The filtrate was concentrated under reduced pressure to give an oily residue, and the oil was then extracted with diethyl ether and filtered to remove any insoluble material. Hexanes were added to the diethyl ether filtrate and the sample was stored at 240 K until colorless block-like crystals formed. IR (cm^{-1}): 3061 w , 2948 w , 2889 w , 1438 m , 1235 m , 1108 m , 1059 m , 934 s , 824 s , 745 m , 720 s , 688 s , 667 m , 624 w . Analysis calculated for $\text{C}_{36}\text{H}_{56}\text{FeSi}_4\text{PO}_4$ (751.98): C, 57.50; H, 7.51. Found: C, 57.38; H, 7.42.

Infrared spectra were recorded on a Shimadzu IRAffinity-1 FTIR Spectrometer using a Pike MIRacle ATR. Elemental analysis was performed by Galbraith Laboratories, Inc. (Knoxville, TN) using a CE-440 Elemental Analyzer.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure was refined as an inversion twin using the twin law $[\bar{1} 0 0, 0 \bar{1} 0, 0 0 \bar{1}]$ and BASF 0.02 (2).

Funding information

Funding for this research was provided by: University College of Pennsylvania State University (grant to Michael T. Hay).

References

- Bruker (2001). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
- Hay, M. T. & Geib, S. J. (2007). *Acta Cryst.* **E63**, m445–m446.
- Hay, M. T., Geib, S. J. & Pettner, D. A. (2009). *Polyhedron*, **28**, 2183–2186.
- Hay, M. T., Hainaut, B. J. & Geib, S. J. (2003). *Inorg. Chem. Commun.* **6**, 431–434.
- Hay, M., Staples, R. & Lee, A. (2012). *Acta Cryst.* **E68**, m1186.
- Jana, T. K., Kumar, D. P., Pradhan, R., Dinda, S., Ghosh, P. N., Simonnet, C., Marrot, J., Imaz, I., Wattiaux, A., Fournès, L., Sutter, J., Sécheresse, F. & Bhattacharyya, R. (2009). *Inorg. Chim. Acta*, **362**, 3583–3594.
- Schmidbaur, H. (1964). *Chem. Ber.* **97**, 842–848.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.

full crystallographic data

IUCrData (2018). 3, x171823 [https://doi.org/10.1107/S2414314617018235]

Tetraphenylphosphonium tetrakis(trimethylsilanolato)ferrate(III)

Michael T. Hay and Hemant P. Yennawar

Tetraphenylphosphonium tetrakis(trimethylsilanolato)ferrate(III)

Crystal data

(C₂₄H₂₀P)[Fe(C₃H₉OSi)₄]

M_r = 751.98

Tetragonal, $\bar{I}4$

a = 12.589 (7) Å

c = 13.689 (7) Å

V = 2169 (3) Å³

Z = 2

F(000) = 802

D_x = 1.151 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 3702 reflections

θ = 2.2–27.0°

μ = 0.53 mm⁻¹

T = 223 K

Block, colorless

0.29 × 0.2 × 0.18 mm

Data collection

Bruker CCD area detector
diffractometer

Graphite monochromator

phi and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2001)

T_{min} = 0.600, *T_{max}* = 0.9

9779 measured reflections

2712 independent reflections

2258 reflections with $I > 2\sigma(I)$

R_{int} = 0.050

θ_{\max} = 28.7°, θ_{\min} = 2.2°

h = -16→16

k = -14→17

l = -18→17

Refinement

Refinement on *F*²

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.036$

wR(*F*²) = 0.078

S = 0.92

2712 reflections

108 parameters

0 restraints

Primary atom site location: structure-invariant
direct methods

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0402P)^2]$

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

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

$\Delta\rho_{\max} = 0.23 \text{ e \AA}^{-3}$

$\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$

Absolute structure: Refined as an inversion twin

Absolute structure parameter: 0.02 (2)

Special details

Experimental. The data collection nominally covered a full sphere of reciprocal space by a combination of 4 sets of ω scans each set at different ϕ and/or 2θ angles and each scan (5 s exposure) covering -0.300° degrees in ω . The crystal to detector distance was 5.82 cm.

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.500000	0.500000	0.500000	0.0378 (2)
Si1	0.51036 (7)	0.69112 (7)	0.66037 (7)	0.0502 (2)
O1	0.46530 (18)	0.61557 (19)	0.57663 (19)	0.0664 (7)
C1	0.4457 (4)	0.6596 (4)	0.7790 (3)	0.0926 (15)
H1A	0.459608	0.586046	0.795930	0.139*
H1B	0.369713	0.670651	0.773541	0.139*
H1C	0.474156	0.705574	0.829510	0.139*
C2	0.6566 (3)	0.6722 (3)	0.6754 (3)	0.0760 (11)
H2A	0.690117	0.670147	0.611577	0.114*
H2B	0.669970	0.605935	0.709348	0.114*
H2C	0.685677	0.730715	0.712920	0.114*
C3	0.4793 (4)	0.8315 (3)	0.6294 (4)	0.0920 (15)
H3A	0.403010	0.842243	0.631577	0.138*
H3B	0.505192	0.847271	0.564214	0.138*
H3C	0.513406	0.878315	0.676095	0.138*
P1	0.500000	0.000000	0.250000	0.0395 (3)
C4	0.4007 (2)	0.0565 (2)	0.3277 (2)	0.0419 (7)
C5	0.4021 (2)	0.1634 (2)	0.3516 (2)	0.0478 (7)
H5	0.452136	0.208548	0.322114	0.057*
C6	0.3310 (3)	0.2040 (3)	0.4180 (3)	0.0563 (8)
H6	0.332071	0.276789	0.433195	0.068*
C7	0.2587 (3)	0.1384 (3)	0.4618 (3)	0.0613 (9)
H7	0.210478	0.165992	0.507764	0.074*
C8	0.2565 (3)	0.0320 (3)	0.4387 (3)	0.0704 (11)
H8	0.205930	-0.012627	0.468087	0.085*
C9	0.3276 (3)	-0.0094 (3)	0.3731 (3)	0.0566 (9)
H9	0.326798	-0.082433	0.359003	0.068*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0392 (3)	0.0392 (3)	0.0351 (4)	0.000	0.000	0.000
Si1	0.0453 (5)	0.0561 (5)	0.0490 (5)	0.0033 (4)	0.0000 (4)	-0.0151 (5)
O1	0.0480 (13)	0.0818 (17)	0.0693 (16)	0.0123 (12)	-0.0067 (12)	-0.0366 (14)
C1	0.095 (3)	0.115 (4)	0.068 (3)	0.008 (3)	0.021 (3)	-0.010 (3)
C2	0.054 (2)	0.102 (3)	0.071 (3)	-0.0019 (19)	-0.014 (2)	0.001 (2)
C3	0.091 (3)	0.069 (3)	0.116 (4)	0.014 (2)	0.006 (3)	-0.007 (3)
P1	0.0383 (5)	0.0383 (5)	0.0420 (8)	0.000	0.000	0.000
C4	0.0460 (16)	0.0404 (15)	0.0394 (16)	-0.0011 (12)	0.0003 (13)	-0.0013 (13)
C5	0.0525 (18)	0.0429 (16)	0.0480 (19)	-0.0070 (13)	0.0036 (15)	0.0001 (14)
C6	0.068 (2)	0.0463 (18)	0.055 (2)	0.0029 (16)	0.0059 (18)	-0.0105 (16)
C7	0.062 (2)	0.061 (2)	0.061 (2)	0.0000 (17)	0.0169 (18)	-0.0111 (17)
C8	0.076 (3)	0.062 (2)	0.073 (3)	-0.0213 (19)	0.033 (2)	-0.009 (2)
C9	0.070 (2)	0.0410 (17)	0.059 (2)	-0.0106 (15)	0.0186 (17)	-0.0051 (15)

Geometric parameters (Å, °)

Fe1—O1 ⁱ	1.846 (2)	C3—H3C	0.9700
Fe1—O1	1.846 (2)	P1—C4 ^{iv}	1.789 (3)
Fe1—O1 ⁱⁱ	1.846 (2)	P1—C4 ^v	1.789 (3)
Fe1—O1 ⁱⁱⁱ	1.846 (2)	P1—C4	1.789 (3)
Si1—O1	1.594 (3)	P1—C4 ^{vi}	1.789 (3)
Si1—C1	1.860 (4)	C4—C5	1.385 (4)
Si1—C2	1.868 (4)	C4—C9	1.386 (4)
Si1—C3	1.860 (4)	C5—H5	0.9400
C1—H1A	0.9700	C5—C6	1.374 (4)
C1—H1B	0.9700	C6—H6	0.9400
C1—H1C	0.9700	C6—C7	1.368 (5)
C2—H2A	0.9700	C7—H7	0.9400
C2—H2B	0.9700	C7—C8	1.377 (5)
C2—H2C	0.9700	C8—H8	0.9400
C3—H3A	0.9700	C8—C9	1.370 (5)
C3—H3B	0.9700	C9—H9	0.9400
O1 ⁱ —Fe1—O1 ⁱⁱ	108.84 (9)	H3A—C3—H3B	109.5
O1 ⁱⁱ —Fe1—O1	110.75 (17)	H3A—C3—H3C	109.5
O1 ⁱ —Fe1—O1	108.84 (9)	H3B—C3—H3C	109.5
O1 ⁱ —Fe1—O1 ⁱⁱⁱ	110.75 (17)	C4 ^{iv} —P1—C4 ^{vi}	110.69 (9)
O1 ⁱⁱⁱ —Fe1—O1	108.84 (9)	C4 ^{vi} —P1—C4 ^v	110.69 (9)
O1 ⁱⁱ —Fe1—O1 ⁱⁱⁱ	108.84 (9)	C4—P1—C4 ^v	110.69 (9)
O1—Si1—C1	110.19 (17)	C4—P1—C4 ^{iv}	110.69 (9)
O1—Si1—C2	110.71 (16)	C4—P1—C4 ^{vi}	107.06 (19)
O1—Si1—C3	109.15 (19)	C4 ^{iv} —P1—C4 ^v	107.06 (19)
C1—Si1—C2	107.9 (2)	C5—C4—P1	121.2 (2)
C1—Si1—C3	108.1 (2)	C5—C4—C9	118.9 (3)
C3—Si1—C2	110.72 (18)	C9—C4—P1	119.6 (2)
Si1—O1—Fe1	142.63 (14)	C4—C5—H5	119.7
Si1—C1—H1A	109.5	C6—C5—C4	120.6 (3)
Si1—C1—H1B	109.5	C6—C5—H5	119.7
Si1—C1—H1C	109.5	C5—C6—H6	120.0
H1A—C1—H1B	109.5	C7—C6—C5	120.0 (3)
H1A—C1—H1C	109.5	C7—C6—H6	120.0
H1B—C1—H1C	109.5	C6—C7—H7	120.0
Si1—C2—H2A	109.5	C6—C7—C8	119.9 (3)
Si1—C2—H2B	109.5	C8—C7—H7	120.0
Si1—C2—H2C	109.5	C7—C8—H8	119.7
H2A—C2—H2B	109.5	C9—C8—C7	120.5 (3)
H2A—C2—H2C	109.5	C9—C8—H8	119.7
H2B—C2—H2C	109.5	C4—C9—H9	120.0
Si1—C3—H3A	109.5	C8—C9—C4	120.0 (3)
Si1—C3—H3B	109.5	C8—C9—H9	120.0
Si1—C3—H3C	109.5		

O1 ⁱ —Fe1—O1—Si1	-62.0 (2)	C4 ^{vi} —P1—C4—C5	96.0 (3)
O1 ⁱⁱ —Fe1—O1—Si1	57.6 (3)	C4 ^{iv} —P1—C4—C9	43.6 (2)
O1 ⁱⁱⁱ —Fe1—O1—Si1	177.2 (3)	C4 ^{vi} —P1—C4—C9	-77.1 (3)
C1—Si1—O1—Fe1	-106.0 (3)	C4 ^v —P1—C4—C9	162.2 (3)
C2—Si1—O1—Fe1	13.3 (4)	C4—C5—C6—C7	0.7 (5)
C3—Si1—O1—Fe1	135.4 (3)	C5—C4—C9—C8	1.6 (5)
P1—C4—C5—C6	-174.3 (2)	C5—C6—C7—C8	-0.6 (6)
P1—C4—C9—C8	174.9 (3)	C6—C7—C8—C9	1.1 (6)
C4 ^v —P1—C4—C5	-24.8 (2)	C7—C8—C9—C4	-1.6 (6)
C4 ^{iv} —P1—C4—C5	-143.3 (3)	C9—C4—C5—C6	-1.2 (5)

Symmetry codes: (i) $y, -x+1, -z+1$; (ii) $-x+1, -y+1, z$; (iii) $-y+1, x, -z+1$; (iv) $-y+1/2, x-1/2, -z+1/2$; (v) $y+1/2, -x+1/2, -z+1/2$; (vi) $-x+1, -y, z$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C6—H6 \cdots O1 ⁱⁱⁱ	0.94	2.47	3.359 (4)	158

Symmetry code: (iii) $-y+1, x, -z+1$.