

Crystal structure of bis(acetylacetonato- κ^2O,O')-(tetrahydrofuran- κO)(trifluoromethanesulfonato- κO)iron(III)

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Keywords: crystal structure; iron(III); acac; triflate; tetrahydrofuran

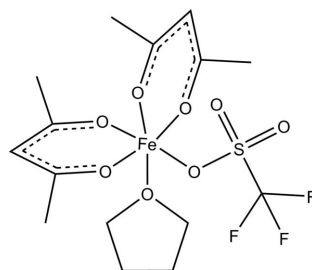
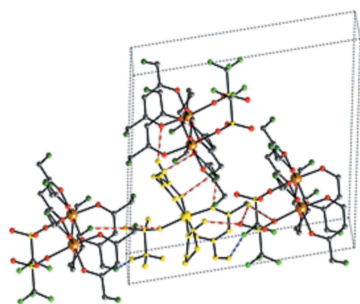
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The mononuclear title complex, $[\text{Fe}(\text{CF}_3\text{O}_3\text{S})(\text{C}_5\text{H}_7\text{O}_2)_2(\text{C}_4\text{H}_8\text{O})]$ or $[\text{Fe}(\text{acac})_2(\text{OTf})(\text{THF})]$ (acac = acetylacetonate; OTf = trifluoromethanesulfonate; THF = tetrahydrofuran), (I), consists of one six-coordinate Fe^{3+} atom in a slightly distorted octahedral environment [$\text{Fe}-\text{O}$ bond-length range = 1.9517 (11)–2.0781 (11) Å]. The triflate ligand was found to be disordered over two sets of sites, with a site-occupancy ratio of 0.622 (16):0.378 (16). Weak intermolecular $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{F}$ hydrogen-bonding interactions generate a two-dimensional supramolecular structure lying parallel to (100). This is only the second crystal structure reported of a mononuclear bis(acetylacetonato)iron(III) complex.

1. Chemical context

Because of its ease-of-handling, relative stability and good solubility in most organic solvents, tris(acetylacetonato)iron(III) $[\text{Fe}(\text{acac})_3]$ is often used as a catalyst or catalyst precursor in iron-catalysed reactions (Sherry & Fürstner, 2008; Zettler *et al.*, 2001). In many applications, the loss or substitution of one or more acetylacetonate ligands from $[\text{Fe}(\text{acac})_3]$ is expected. However, the substitution of a single acetylacetonato ligand is rarely observed. Relevant examples include protonations of $\text{Fe}(\text{acac})_3$ with oxalic acid (Fujino *et al.*, 2004) and hydrochloric acid (Lindley & Smith, 1970) to form $[\text{Fe}(\text{acac})_2]_2(\mu\text{-C}_2\text{O}_4)$ and $[\text{Fe}(\text{acac})_2\text{Cl}]$, respectively. The dinuclear alkoxides, $[\text{Fe}(\text{acac})_2(\mu\text{-OR})]$ are also known (Chiari *et al.*, 1984; Leluk *et al.*, 1992; Wu *et al.*, 1972). We now report that the addition of triflic acid to a THF solution of $[\text{Fe}(\text{acac})_3]$ results in the formation of a mononuclear bis(acetylacetonato)iron(III) complex, $[\text{Fe}(\text{acac})_2(\text{OTf})(\text{THF})]$, the title compound (I) whose structure is reported herein. This compound is a rare bis(acetylacetonato)iron(III) complex that has been crystallographically characterized.



2. Structural commentary

The molecular structure of the mononuclear complex (I) (Fig. 1) consists of one six-coordinate Fe^{3+} atom in a slightly

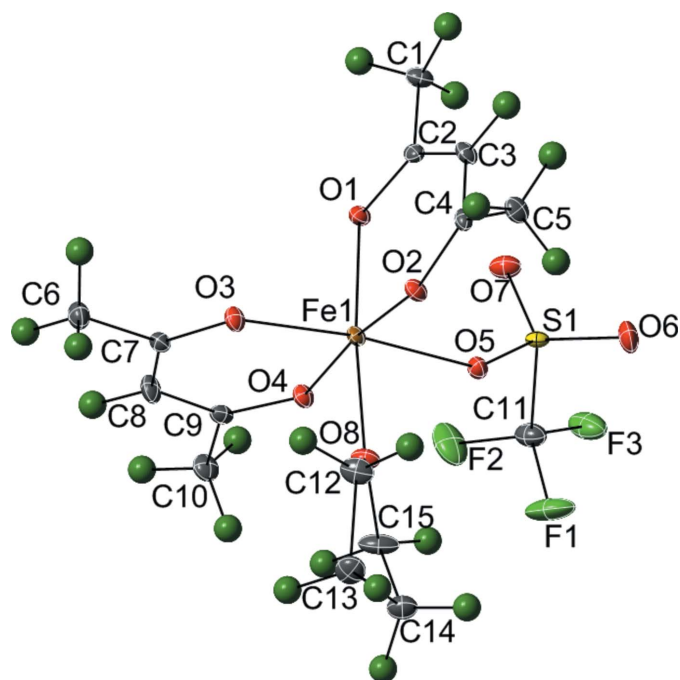


Figure 1
A molecule plot showing the atom numbering, with 35% probability ellipsoids for non-H atoms and spheres of arbitrary size for H atoms. Only the major component of the disordered triflate ligand is shown.

distorted octahedral FeO_6 environment. The coordination sphere of the metal comprises four oxygen atoms from two κ^2 -acac ligands [$\text{Fe}-\text{O}_{\text{acac}}$ range = 1.9517 (11)–1.9762 (11) Å], one oxygen atom of a THF solvate molecule [$\text{Fe1}-\text{O8}$ = 2.0781 (11) Å] and one oxygen atom of a disordered triflate anion [$\text{Fe1}-\text{O5}$ = 2.063 (4) Å or $\text{Fe1}-\text{O5B}$ = 2.066 (6) Å] (Table 1). The disorder in the triflate ligand was found to be 0.622 (16):0.378 (16). The angles around Fe1 deviate from the ideal octahedral angles of 90 and 180°, the *cis* angles range from 84.63 (5)° to 98.09 (5)° and the *trans* angles range from 172.60 (5)° to 174.9 (6)°.

3. Supramolecular features

There are no significant supramolecular features to discuss in the extended structure of (I). There are weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\text{F}$ intermolecular hydrogen-bonding interactions resulting in the formation of two-dimensional layers parallel to the (100) plane (Fig. 2*a,b*). A series of $\text{C}_{\text{methyl}}-\text{H}\cdots\text{O}_{\text{acac}}$, $\text{C}_{\text{methyl}}-\text{H}\cdots\text{O}_{\text{triflate}}$, $\text{C}_{\text{methyl}}-\text{H}\cdots\text{F}_{\text{triflate}}$, $\text{C}_{\text{THF}}-\text{H}\cdots\text{O}_{\text{triflate}}$, and $\text{C}_{\text{THF}}-\text{H}\cdots\text{F}_{\text{triflate}}$ interactions make up the layers, the details of these interactions are presented in Table 2. Each molecule connects to six neighboring molecules through various combinations of these interactions, Fig. 2*c,d*.

4. Database survey

Only one other mononuclear bis(acetylacetonato)iron(III) complex has been characterized crystallographically, [$\text{Fe}(\text{acac})_2\text{Cl}$] (Lindley & Smith, 1970). This complex

Table 1
Selected bond lengths (Å).

$\text{Fe1}-\text{O1}$	1.9517 (11)	$\text{Fe1}-\text{O8}$	2.0781 (11)
$\text{Fe1}-\text{O4}$	1.9651 (11)	$\text{Fe1}-\text{O5}$	2.063 (4)
$\text{Fe1}-\text{O3}$	1.9742 (11)	$\text{Fe1}-\text{O5B}$	2.066 (6)
$\text{Fe1}-\text{O2}$	1.9762 (11)		

Table 2
Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C1}-\text{H1B}\cdots\text{O3}^{\text{i}}$	0.98	2.53	3.370 (2)	144
$\text{C5}-\text{H5A}\cdots\text{O1}^{\text{ii}}$	0.98	2.60	3.539 (2)	161
$\text{C5}-\text{H5B}\cdots\text{O6B}^{\text{iii}}$	0.98	2.56	3.471 (12)	154
$\text{C6}-\text{H6A}\cdots\text{O5}^{\text{iv}}$	0.98	2.63	3.429 (9)	138
$\text{C6}-\text{H6A}\cdots\text{O6}^{\text{iv}}$	0.98	2.58	3.436 (10)	145
$\text{C10}-\text{H10B}\cdots\text{F3}^{\text{v}}$	0.98	2.56	3.214 (6)	124
$\text{C12}-\text{H12A}\cdots\text{O6}^{\text{iv}}$	0.99	2.51	3.321 (7)	138
$\text{C12}-\text{H12A}\cdots\text{O6B}^{\text{iv}}$	0.99	2.60	3.423 (11)	140
$\text{C14}-\text{H14A}\cdots\text{O7B}^{\text{vi}}$	0.99	2.63	3.411 (10)	136
$\text{C14}-\text{H14B}\cdots\text{F2B}^{\text{vii}}$	0.99	2.50	3.316 (6)	139

Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (vi) $x, y+1, z$; (vii) $-x+2, y+\frac{1}{2}, -z+\frac{3}{2}$.

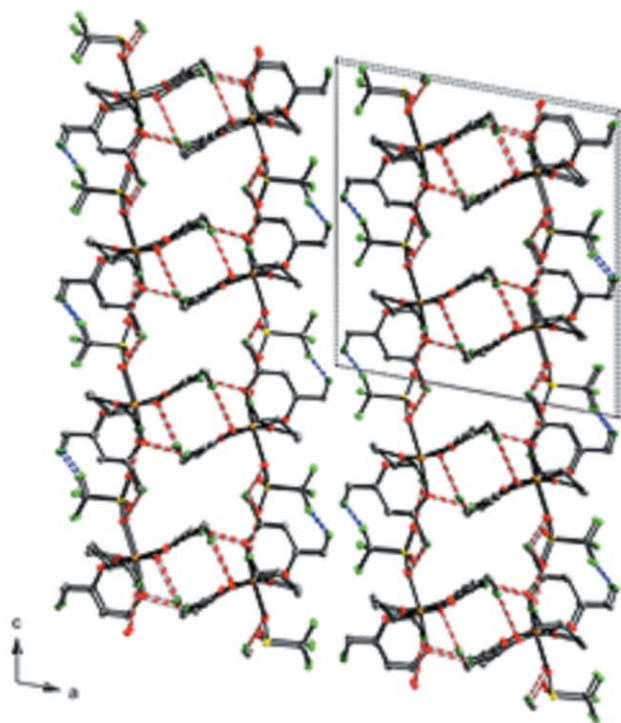
comprises a five-coordinate iron(III) atom in a square-pyramidal geometry. The $\text{Fe}-\text{O}$ distance reported is 1.95 (1) Å, which is comparable to the average $\text{Fe}-\text{O}_{\text{acac}}$ distance in (I) of 1.9668 Å. A search of the Cambridge Structural Database (Groom & Allen, 2014) reveals twelve bis(acetylacetonato)iron(III) complexes with a $\text{Fe}-\text{O}_{\text{acac}}$ range of 1.945–2.062 Å.

A survey of the database for similar complexes with other transition metals yields one mononuclear bis(acac)-triflate complex, [$\text{Os}(\text{acac})_2(\text{C}_6\text{H}_5)(\text{OTf})$] (Young *et al.*, 2011). There is also only one mononuclear bis(acac)-THF complex, [$\text{V}(\text{acac})_2(\text{Mes})(\text{THF})$] (Mes = mesityl; Imhof & Seidel, 2006). There are six bis(acac)-bis(THF) complexes; three mononuclear (Baisch & Poli, 2008; Döring *et al.*, 1992; Langer *et al.*, 2007), two dinuclear (Baisch & Poli, 2008; Döring *et al.*, 1992) and one heterometallic tetranuclear (Döring *et al.*, 2006).

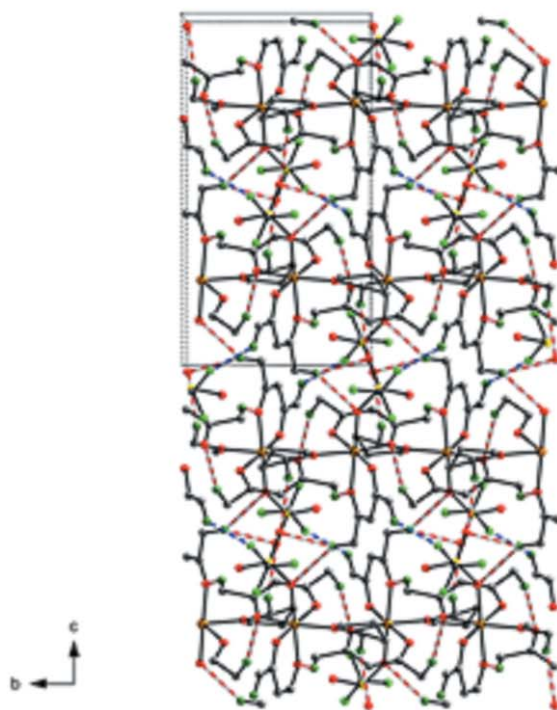
5. Synthesis and crystallization

Triflic acid (251 µL, 0.24 g, 1 equiv) was added to a solution of [$\text{Fe}(\text{acac})_3$] (1 g, 2.83 mmol, 1 equiv) in dry THF (5 mL). The resulting purple–red solution was stirred at room temperature for 1 h. The reaction mixture was then concentrated under vacuum to a volume of approximately 2 mL, and 20 mL of pentane was added. A dark purple–red microcrystalline solid precipitated. The mixture was filtered through a glass-frit and the microcrystalline solid was dried under vacuum (1.25 g, 2.63 mmol, 93%). Crystals suitable for X-ray diffraction were grown by slow diffusion of pentane into a THF solution of the purple–red solid. CH analysis calculated for $\text{C}_{15}\text{H}_{22}\text{F}_3\text{FeO}_8\text{S}$ (MW: 475.235): C 37.91%; H 4.67%. Found: C 37.69%; H, 4.45%.

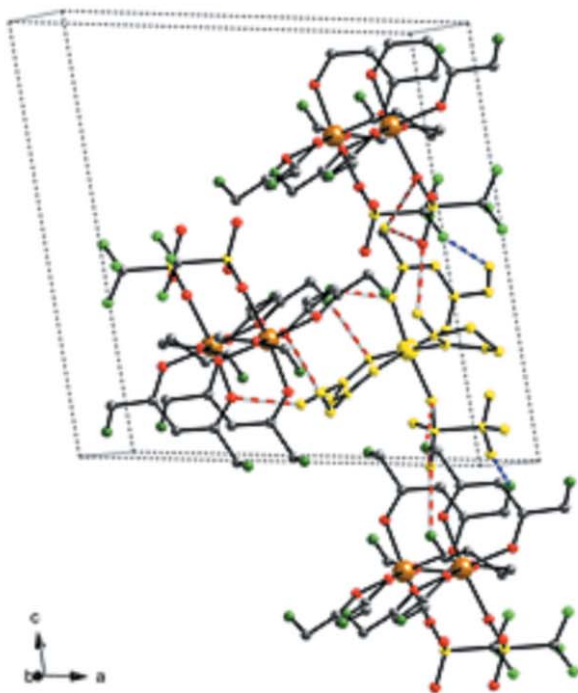
(a)



(b)



(c)



(d)

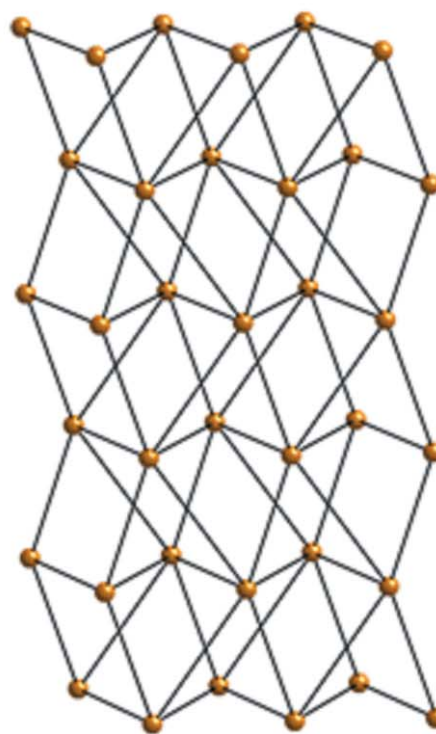


Figure 2

A view of the extended structure of (I) (a) along the *b* axis showing two neighboring layers; (b) along the *a* axis showing one two-dimensional layer; (c) showing the highlighted molecule connecting to six neighboring molecules; and (d) reduced to a ball-and-stick representation, orange balls represent one molecule of (I) connecting to six neighbors. H...O interactions are shown as red dashed lines, H...F interactions are shown as blue dashed lines. Only the major component of the disordered triflate is shown, and all H atoms except those that participate in the interactions are omitted in parts (a)–(c).

Table 3
Experimental details.

Crystal data	
Chemical formula	[Fe(CF ₃ O ₃ S)(C ₅ H ₇ O ₂) ₂ (C ₄ H ₈ O)]
<i>M</i> _r	475.23
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Temperature (K)	103
<i>a</i> , <i>b</i> , <i>c</i> (Å)	15.0118 (8), 8.4523 (4), 15.9842 (9)
β (°)	100.451 (2)
<i>V</i> (Å ³)	1994.50 (18)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.93
Crystal size (mm)	0.77 × 0.09 × 0.08
Data collection	
Diffractometer	Bruker D8 Venture/Photon 100
Absorption correction	Integration (<i>SADABS</i> ; Bruker, 2013)
<i>T</i> _{min} , <i>T</i> _{max}	0.720, 0.955
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	48981, 4417, 3800
<i>R</i> _{int}	0.058
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.642
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.066, 1.06
No. of reflections	4417
No. of parameters	330
No. of restraints	344
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.29, -0.38

Computer programs: *APEX2*, *SAINT*, *XPREP*, *SADABS*, *TWINABS* and *XCIF* (Bruker, 2013), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2015), *CrystalMaker* (CrystalMaker, 1994) and *pubCIF* (Westrip, 2010).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. A structural model consisting of the target molecule was developed. The triflate ion is disordered over two positions, with refined site-occupancies of 0.622 (16) and 0.378 (16). The equivalent Fe–O, O–S, S–C, and C–F distances were restrained to be similar (s.u. = 0.01 Å). The disordered atoms were restrained to behave relatively isotropically. Similar displacement amplitudes were imposed on disordered sites overlapping by less than the sum of van der Waals radii. Methyl H atom positions were opti-

mized by rotation about *R*–C bonds with idealized C–H, *R* ···H and H ···H distances and included as riding idealized contributors [C–H_{methyl} = 0.98 Å with *U*_{iso} = 1.5*U*_{eq}(C)]. Remaining H atoms were also included as riding idealized contributors [C–H_{methylene} = 0.99 Å and C–H_{aromatic} = 0.95 Å, both with *U*_{iso} = 1.2*U*_{eq}(C)].

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Crystal structure of bis(acetylacetonato- κ^2O,O')(tetrahydrofuran- κO)(trifluoromethanesulfonato- κO)iron(III)

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Computing details

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINTE* (Bruker, 2013); data reduction: *SAINTE*, *XPREP*, *SADABS* and *TWINABS* (Bruker, 2013); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *CrystalMaker* (*CrystalMaker*, 1994); software used to prepare material for publication: *XCIF* (Bruker, 2013) and *pubCIF* (Westrip, 2010).

Bis(acetylacetonato- κ^2O,O')(tetrahydrofuran- κO)(trifluoromethanesulfonato- κO)iron(III)

Crystal data

[Fe(CF₃O₃S)(C₅H₇O₂)₂(C₄H₈O)]

$M_r = 475.23$

Monoclinic, $P2_1/c$

$a = 15.0118$ (8) Å

$b = 8.4523$ (4) Å

$c = 15.9842$ (9) Å

$\beta = 100.451$ (2)°

$V = 1994.50$ (18) Å³

$Z = 4$

$F(000) = 980$

$D_x = 1.583$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9821 reflections

$\theta = 2.6$ – 27.1 °

$\mu = 0.93$ mm⁻¹

$T = 103$ K

Needle, red

$0.77 \times 0.09 \times 0.08$ mm

Data collection

Bruker D8 Venture/Photon 100
diffractometer

Radiation source: microfocus sealed tube

Multilayer mirrors monochromator

profile data from φ and ω scans

Absorption correction: integration

(*SADABS*; Bruker, 2013)

$T_{\min} = 0.720$, $T_{\max} = 0.955$

48981 measured reflections

4417 independent reflections

3800 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 27.2$ °, $\theta_{\min} = 2.6$ °

$h = -19 \rightarrow 19$

$k = -10 \rightarrow 10$

$l = -20 \rightarrow 20$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.025$

$wR(F^2) = 0.066$

$S = 1.06$

4417 reflections

330 parameters

344 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.030P)^2 + 1.245P]$

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

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

$\Delta\rho_{\max} = 0.29$ e Å⁻³

$\Delta\rho_{\min} = -0.38$ e Å⁻³

Special details

Experimental. One distinct cell was identified using *APEX2* (Bruker, 2013). Six frame series were integrated and filtered for statistical outliers using *SAINT* (Bruker, 2013) then corrected for absorption by integration using *SAINT/SADABS* (Bruker, 2013) to sort, merge, and scale the combined data. No decay correction was applied.

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

Refinement. Structure was phased by direct methods (Sheldrick, 2008). Systematic conditions suggested the unambiguous space group. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2 . The final map had no significant features. A final analysis of variance between observed and calculated structure factors showed little dependence on amplitude or resolution.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Fe1	0.70581 (2)	0.58797 (3)	0.74733 (2)	0.01158 (7)	
O1	0.63555 (7)	0.39298 (13)	0.72713 (7)	0.0148 (2)	
O2	0.59623 (7)	0.70589 (13)	0.69469 (7)	0.0149 (2)	
C1	0.53914 (11)	0.19970 (19)	0.65236 (11)	0.0190 (3)	
H1A	0.5792	0.1539	0.6167	0.028*	
H1B	0.4762	0.1933	0.6225	0.028*	
H1C	0.5457	0.1409	0.7060	0.028*	
C2	0.56412 (10)	0.36918 (19)	0.67064 (10)	0.0142 (3)	
C3	0.51150 (11)	0.48966 (19)	0.62755 (10)	0.0161 (3)	
H3	0.4612	0.4605	0.5852	0.019*	
C4	0.52805 (10)	0.65102 (19)	0.64266 (9)	0.0139 (3)	
C5	0.46288 (11)	0.7717 (2)	0.59819 (11)	0.0189 (3)	
H5A	0.4358	0.8302	0.6403	0.028*	
H5B	0.4150	0.7183	0.5583	0.028*	
H5C	0.4952	0.8455	0.5670	0.028*	
O3	0.68185 (7)	0.60779 (13)	0.86430 (7)	0.0160 (2)	
O4	0.82353 (7)	0.49312 (13)	0.79526 (7)	0.0146 (2)	
C6	0.69073 (12)	0.5923 (2)	1.01300 (10)	0.0207 (4)	
H6A	0.6823	0.7058	1.0215	0.031*	
H6B	0.7315	0.5487	1.0625	0.031*	
H6C	0.6320	0.5386	1.0062	0.031*	
C7	0.73100 (11)	0.56757 (18)	0.93464 (10)	0.0145 (3)	
C8	0.81768 (11)	0.5026 (2)	0.94177 (11)	0.0205 (4)	
H8	0.8498	0.4788	0.9972	0.025*	
C9	0.85978 (11)	0.47054 (18)	0.87341 (10)	0.0143 (3)	
C10	0.95457 (11)	0.4060 (2)	0.88703 (11)	0.0211 (4)	
H10A	0.9567	0.3141	0.8501	0.032*	
H10B	0.9730	0.3741	0.9466	0.032*	
H10C	0.9959	0.4878	0.8733	0.032*	
S1	0.7575 (2)	0.4546 (5)	0.5659 (2)	0.0133 (7)	0.622 (16)
O5	0.7471 (8)	0.5722 (10)	0.6313 (4)	0.0148 (14)	0.622 (16)
O6	0.7263 (6)	0.5123 (11)	0.4815 (4)	0.0255 (14)	0.622 (16)
O7	0.7340 (4)	0.2959 (7)	0.5840 (5)	0.0218 (11)	0.622 (16)

C11	0.8807 (3)	0.4490 (8)	0.5760 (4)	0.0251 (11)	0.622 (16)
F1	0.9134 (4)	0.5931 (7)	0.5691 (5)	0.0487 (14)	0.622 (16)
F2	0.9202 (3)	0.3903 (10)	0.6507 (2)	0.0451 (12)	0.622 (16)
F3	0.9047 (7)	0.3580 (11)	0.5158 (6)	0.0374 (15)	0.622 (16)
S1B	0.7611 (4)	0.4453 (9)	0.5676 (3)	0.0166 (12)	0.378 (16)
O5B	0.7429 (13)	0.5656 (16)	0.6296 (7)	0.014 (2)	0.378 (16)
O6B	0.7140 (9)	0.4806 (17)	0.4836 (6)	0.0209 (19)	0.378 (16)
O7B	0.7585 (8)	0.2869 (11)	0.5971 (9)	0.027 (2)	0.378 (16)
C11B	0.8794 (5)	0.4866 (12)	0.5638 (6)	0.0249 (18)	0.378 (16)
F1B	0.8914 (6)	0.6304 (9)	0.5356 (7)	0.0424 (16)	0.378 (16)
F2B	0.9310 (4)	0.4709 (16)	0.6402 (4)	0.047 (2)	0.378 (16)
F3B	0.9104 (11)	0.3852 (18)	0.5118 (9)	0.037 (2)	0.378 (16)
O8	0.76794 (8)	0.80858 (13)	0.75681 (7)	0.0171 (2)	
C12	0.72268 (12)	0.9548 (2)	0.77383 (13)	0.0237 (4)	
H12A	0.6923	0.9419	0.8235	0.028*	
H12B	0.6768	0.9859	0.7239	0.028*	
C13	0.79668 (13)	1.0771 (2)	0.79186 (12)	0.0252 (4)	
H13A	0.8229	1.0812	0.8533	0.030*	
H13B	0.7738	1.1834	0.7728	0.030*	
C14	0.86588 (12)	1.0189 (2)	0.74034 (12)	0.0238 (4)	
H14A	0.8492	1.0511	0.6800	0.029*	
H14B	0.9272	1.0593	0.7639	0.029*	
C15	0.86120 (12)	0.8415 (2)	0.74971 (14)	0.0291 (4)	
H15A	0.8771	0.7876	0.6994	0.035*	
H15B	0.9032	0.8055	0.8012	0.035*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.00926 (11)	0.01369 (11)	0.01071 (11)	0.00065 (8)	-0.00107 (8)	-0.00028 (8)
O1	0.0115 (5)	0.0167 (5)	0.0150 (5)	-0.0007 (4)	-0.0010 (4)	0.0020 (4)
O2	0.0116 (5)	0.0162 (5)	0.0152 (6)	0.0010 (4)	-0.0023 (4)	-0.0011 (4)
C1	0.0140 (8)	0.0176 (8)	0.0242 (9)	-0.0032 (6)	0.0002 (7)	-0.0022 (7)
C2	0.0111 (7)	0.0194 (8)	0.0129 (7)	-0.0026 (6)	0.0044 (6)	-0.0020 (6)
C3	0.0118 (8)	0.0206 (8)	0.0142 (8)	-0.0003 (6)	-0.0021 (6)	-0.0024 (6)
C4	0.0103 (7)	0.0216 (8)	0.0098 (7)	0.0018 (6)	0.0019 (6)	0.0001 (6)
C5	0.0155 (8)	0.0207 (8)	0.0182 (8)	0.0039 (6)	-0.0027 (7)	0.0004 (6)
O3	0.0127 (5)	0.0222 (6)	0.0123 (5)	0.0033 (5)	-0.0002 (4)	0.0000 (4)
O4	0.0117 (5)	0.0179 (5)	0.0132 (5)	0.0025 (4)	-0.0006 (4)	-0.0004 (4)
C6	0.0208 (9)	0.0269 (9)	0.0142 (8)	0.0013 (7)	0.0031 (7)	-0.0014 (7)
C7	0.0154 (8)	0.0140 (7)	0.0133 (7)	-0.0024 (6)	0.0002 (6)	-0.0011 (6)
C8	0.0161 (8)	0.0308 (9)	0.0126 (8)	0.0047 (7)	-0.0025 (6)	0.0030 (7)
C9	0.0118 (8)	0.0116 (7)	0.0178 (8)	-0.0010 (6)	-0.0017 (6)	0.0015 (6)
C10	0.0140 (8)	0.0265 (9)	0.0211 (8)	0.0050 (7)	-0.0013 (7)	0.0018 (7)
S1	0.0083 (9)	0.0132 (9)	0.0184 (12)	-0.0024 (7)	0.0027 (7)	-0.0013 (7)
O5	0.017 (2)	0.015 (2)	0.012 (2)	-0.0008 (19)	0.0022 (19)	-0.0018 (19)
O6	0.031 (3)	0.034 (3)	0.0109 (15)	0.002 (2)	0.0008 (14)	-0.0019 (14)
O7	0.019 (2)	0.0163 (17)	0.032 (3)	-0.0012 (15)	0.0075 (19)	-0.0042 (13)

C11	0.0187 (18)	0.028 (2)	0.030 (2)	-0.0036 (14)	0.0092 (15)	-0.0096 (16)
F1	0.032 (2)	0.040 (2)	0.081 (3)	-0.0199 (16)	0.030 (2)	-0.021 (2)
F2	0.0209 (13)	0.076 (3)	0.0348 (13)	0.0163 (16)	-0.0044 (10)	-0.0075 (17)
F3	0.025 (2)	0.047 (3)	0.043 (2)	0.0016 (19)	0.0147 (16)	-0.0223 (19)
S1B	0.023 (2)	0.0207 (19)	0.0045 (16)	0.0033 (12)	-0.0006 (12)	-0.0060 (12)
O5B	0.016 (4)	0.013 (4)	0.014 (4)	0.000 (3)	0.003 (3)	-0.002 (3)
O6B	0.019 (3)	0.030 (4)	0.012 (3)	-0.009 (3)	-0.0012 (19)	-0.003 (2)
O7B	0.036 (5)	0.016 (2)	0.029 (4)	0.011 (3)	0.010 (4)	0.004 (2)
C11B	0.018 (3)	0.034 (4)	0.022 (3)	0.000 (3)	0.001 (2)	-0.011 (3)
F1B	0.029 (3)	0.038 (3)	0.065 (4)	-0.017 (2)	0.021 (3)	-0.006 (2)
F2B	0.019 (2)	0.082 (5)	0.036 (3)	0.013 (3)	-0.0121 (17)	-0.020 (3)
F3B	0.022 (3)	0.049 (5)	0.044 (4)	-0.002 (3)	0.015 (3)	-0.023 (3)
O8	0.0116 (5)	0.0136 (5)	0.0260 (6)	0.0004 (4)	0.0029 (5)	-0.0043 (5)
C12	0.0208 (9)	0.0162 (8)	0.0346 (10)	0.0029 (7)	0.0063 (8)	-0.0087 (7)
C13	0.0318 (10)	0.0166 (8)	0.0279 (10)	-0.0043 (7)	0.0075 (8)	-0.0068 (7)
C14	0.0225 (9)	0.0190 (8)	0.0299 (10)	-0.0038 (7)	0.0050 (8)	-0.0013 (7)
C15	0.0131 (9)	0.0202 (9)	0.0541 (13)	-0.0033 (7)	0.0066 (8)	-0.0066 (9)

Geometric parameters (Å, °)

Fe1—O1	1.9517 (11)	C10—H10A	0.9800
Fe1—O4	1.9651 (11)	C10—H10B	0.9800
Fe1—O3	1.9742 (11)	C10—H10C	0.9800
Fe1—O2	1.9762 (11)	S1—O7	1.430 (4)
Fe1—O8	2.0781 (11)	S1—O6	1.431 (4)
Fe1—O5	2.063 (4)	S1—O5	1.472 (4)
Fe1—O5B	2.066 (6)	S1—C11	1.829 (4)
O1—C2	1.2862 (19)	C11—F1	1.324 (5)
O2—C4	1.2827 (19)	C11—F2	1.329 (5)
C1—C2	1.496 (2)	C11—F3	1.332 (4)
C1—H1A	0.9800	S1B—O7B	1.422 (6)
C1—H1B	0.9800	S1B—O6B	1.431 (6)
C1—H1C	0.9800	S1B—O5B	1.479 (6)
C2—C3	1.392 (2)	S1B—C11B	1.822 (6)
C3—C4	1.399 (2)	C11B—F1B	1.319 (7)
C3—H3	0.9500	C11B—F2B	1.330 (7)
C4—C5	1.500 (2)	C11B—F3B	1.335 (6)
C5—H5A	0.9800	O8—C15	1.452 (2)
C5—H5B	0.9800	O8—C12	1.4596 (19)
C5—H5C	0.9800	C12—C13	1.506 (2)
O3—C7	1.2740 (19)	C12—H12A	0.9900
O4—C9	1.2830 (19)	C12—H12B	0.9900
C6—C7	1.501 (2)	C13—C14	1.520 (3)
C6—H6A	0.9800	C13—H13A	0.9900
C6—H6B	0.9800	C13—H13B	0.9900
C6—H6C	0.9800	C14—C15	1.509 (2)
C7—C8	1.398 (2)	C14—H14A	0.9900
C8—C9	1.385 (2)	C14—H14B	0.9900

C8—H8	0.9500	C15—H15A	0.9900
C9—C10	1.503 (2)	C15—H15B	0.9900
O1—Fe1—O4	98.09 (5)	C9—C10—H10A	109.5
O1—Fe1—O3	92.44 (5)	C9—C10—H10B	109.5
O4—Fe1—O3	88.33 (5)	H10A—C10—H10B	109.5
O1—Fe1—O2	88.42 (5)	C9—C10—H10C	109.5
O4—Fe1—O2	172.76 (5)	H10A—C10—H10C	109.5
O3—Fe1—O2	94.58 (5)	H10B—C10—H10C	109.5
O1—Fe1—O5	92.2 (3)	O7—S1—O6	117.4 (4)
O4—Fe1—O5	85.9 (3)	O7—S1—O5	115.3 (4)
O3—Fe1—O5	173.1 (3)	O6—S1—O5	112.4 (4)
O2—Fe1—O5	90.7 (3)	O7—S1—C11	103.9 (3)
O1—Fe1—O5B	89.9 (4)	O6—S1—C11	104.2 (4)
O4—Fe1—O5B	86.9 (5)	O5—S1—C11	101.0 (4)
O3—Fe1—O5B	174.9 (6)	S1—O5—Fe1	140.4 (5)
O2—Fe1—O5B	89.9 (5)	F1—C11—F2	107.9 (4)
O1—Fe1—O8	172.60 (5)	F1—C11—F3	108.5 (5)
O4—Fe1—O8	88.72 (5)	F2—C11—F3	107.4 (5)
O3—Fe1—O8	90.64 (5)	F1—C11—S1	110.6 (3)
O2—Fe1—O8	84.63 (5)	F2—C11—S1	111.6 (4)
O5—Fe1—O8	85.4 (2)	F3—C11—S1	110.7 (5)
O5B—Fe1—O8	87.5 (4)	O7B—S1B—O6B	118.0 (7)
C2—O1—Fe1	127.22 (10)	O7B—S1B—O5B	114.0 (7)
C4—O2—Fe1	126.75 (10)	O6B—S1B—O5B	111.4 (8)
C2—C1—H1A	109.5	O7B—S1B—C11B	106.1 (5)
C2—C1—H1B	109.5	O6B—S1B—C11B	104.3 (6)
H1A—C1—H1B	109.5	O5B—S1B—C11B	101.0 (7)
C2—C1—H1C	109.5	S1B—O5B—Fe1	141.8 (8)
H1A—C1—H1C	109.5	F1B—C11B—F2B	108.2 (6)
H1B—C1—H1C	109.5	F1B—C11B—F3B	107.2 (8)
O1—C2—C3	123.98 (15)	F2B—C11B—F3B	107.3 (9)
O1—C2—C1	115.74 (14)	F1B—C11B—S1B	112.5 (5)
C3—C2—C1	120.28 (14)	F2B—C11B—S1B	111.0 (5)
C2—C3—C4	124.09 (15)	F3B—C11B—S1B	110.5 (8)
C2—C3—H3	118.0	C15—O8—C12	109.89 (12)
C4—C3—H3	118.0	C15—O8—Fe1	126.35 (10)
O2—C4—C3	124.06 (14)	C12—O8—Fe1	123.75 (10)
O2—C4—C5	115.87 (14)	O8—C12—C13	105.35 (14)
C3—C4—C5	120.06 (14)	O8—C12—H12A	110.7
C4—C5—H5A	109.5	C13—C12—H12A	110.7
C4—C5—H5B	109.5	O8—C12—H12B	110.7
H5A—C5—H5B	109.5	C13—C12—H12B	110.7
C4—C5—H5C	109.5	H12A—C12—H12B	108.8
H5A—C5—H5C	109.5	C12—C13—C14	103.12 (14)
H5B—C5—H5C	109.5	C12—C13—H13A	111.1
C7—O3—Fe1	129.59 (10)	C14—C13—H13A	111.1
C9—O4—Fe1	129.27 (10)	C12—C13—H13B	111.1

C7—C6—H6A	109.5	C14—C13—H13B	111.1
C7—C6—H6B	109.5	H13A—C13—H13B	109.1
H6A—C6—H6B	109.5	C15—C14—C13	102.66 (15)
C7—C6—H6C	109.5	C15—C14—H14A	111.2
H6A—C6—H6C	109.5	C13—C14—H14A	111.2
H6B—C6—H6C	109.5	C15—C14—H14B	111.2
O3—C7—C8	123.95 (15)	C13—C14—H14B	111.2
O3—C7—C6	116.28 (14)	H14A—C14—H14B	109.1
C8—C7—C6	119.77 (15)	O8—C15—C14	105.13 (14)
C9—C8—C7	124.32 (15)	O8—C15—H15A	110.7
C9—C8—H8	117.8	C14—C15—H15A	110.7
C7—C8—H8	117.8	O8—C15—H15B	110.7
O4—C9—C8	124.44 (15)	C14—C15—H15B	110.7
O4—C9—C10	114.74 (14)	H15A—C15—H15B	108.8
C8—C9—C10	120.83 (15)		

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>
C1—H1 <i>B</i> ...O3 ⁱ	0.98	2.53	3.370 (2)	144
C5—H5 <i>A</i> ...O1 ⁱⁱ	0.98	2.60	3.539 (2)	161
C5—H5 <i>B</i> ...O6 <i>B</i> ⁱⁱⁱ	0.98	2.56	3.471 (12)	154
C6—H6 <i>A</i> ...O5 ^{iv}	0.98	2.63	3.429 (9)	138
C6—H6 <i>A</i> ...O6 ^{iv}	0.98	2.58	3.436 (10)	145
C10—H10 <i>B</i> ...F3 ^v	0.98	2.56	3.214 (6)	124
C12—H12 <i>A</i> ...O6 ^{iv}	0.99	2.51	3.321 (7)	138
C12—H12 <i>A</i> ...O6 <i>B</i> ^{iv}	0.99	2.60	3.423 (11)	140
C14—H14 <i>A</i> ...O7 <i>B</i> ^{vi}	0.99	2.63	3.411 (10)	136
C14—H14 <i>B</i> ...F2 <i>B</i> ^{vii}	0.99	2.50	3.316 (6)	139

Symmetry codes: (i) $-x+1, y-1/2, -z+3/2$; (ii) $-x+1, y+1/2, -z+3/2$; (iii) $-x+1, -y+1, -z+1$; (iv) $x, -y+3/2, z+1/2$; (v) $x, -y+1/2, z+1/2$; (vi) $x, y+1, z$; (vii) $-x+2, y+1/2, -z+3/2$.