

An unusual example of a linearly coordinated acetone ligand in a six-coordinate iron(II) complex

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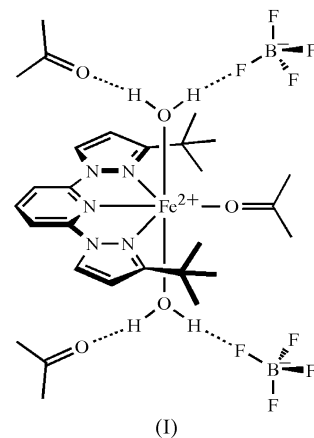
The title compound, acetonediaqua[2,6-bis(3-*tert*-butylpyrazol-1-yl)pyridine]iron(II) bis(tetrafluoroborate) acetone disolvate, $[\text{Fe}(\text{C}_{19}\text{H}_{25}\text{N}_5)(\text{C}_3\text{H}_6\text{O})(\text{H}_2\text{O})_2](\text{BF}_4)_2 \cdot 2\text{C}_3\text{H}_6\text{O}$, contains a C_2 -symmetric six-coordinate complex dication, with an acetone ligand in its equatorial plane that is linearly coordinated by symmetry ($\text{Fe}-\text{O}=\text{CMe}_2 = 180^\circ$). This is a consequence of close steric contacts between the coordinated carbonyl group and the two distal *tert*-butyl substituents on the tridentate ligand.

Comment

We are studying the chemistry of homoleptic iron(II) complexes of 2,6-dipyrazolylpyridine and 2,6-dipyrazolylpyridazine derivatives (Halcrow, 2005). Compounds of this type sometimes exhibit an unusual angular Jahn–Teller distortion, in which the metal coordination is severely twisted from its ideal near-octahedral geometry (Holland *et al.*, 2002; Elhaik *et al.*, 2005, 2006; Kilner & Halcrow, 2006). We have been looking for more examples of this phenomenon and decided to examine the iron(II) chemistry of 2,6-bis(3-*tert*-butylpyrazol-1-yl)pyridine (*L*) to determine if the bulky ligand substituents might enforce a structural distortion onto an $[\text{FeL}_2]^{2+}$ centre. In fact, as we had already observed in its copper chemistry (Solanki *et al.*, 2002), *L* proved too bulky to allow $[\text{FeL}_2]^{2+}$ to form. Hence, when hydrated $\text{Fe}(\text{BF}_4)_2$ and two molar equivalents of *L* were reacted in MeOH, MeCN or MeNO₂, the resulting yellow solutions only yielded single crystals of unreacted *L* (Halcrow, 2005) and/or small amounts of intractable powder when layered with Et₂O. A pure iron-containing product was only obtained when these reactions were performed in acetone, giving near-colourless crystals of *trans*- $[\text{FeL}(\text{OH}_2)_2(\text{OCMe}_2)](\text{BF}_4)_2 \cdot 2\text{Me}_2\text{CO}$, (I). This compound was obtained in pure form when $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and *L* were reacted in a 1:1 molar ratio under the same conditions.

The complex dication in (I) spans a crystallographic C_2 axis passing through atoms Fe1, N2, C5, O16 and C17 (Fig. 1). The bond lengths to Fe1 are in the range expected for a high-spin

iron(II) centre (but see below), while the bond angles are close to those of an ideal octahedron, except for the restricted



74.50 (4)° bite angle of the *L* ligand (Table 1). The metal coordination is completed by an acetone ligand occupying the fourth equatorial coordination site and by two axial water ligands. Notably, the acetone ligand is coordinated in a linear fashion, the Fe1–O16–C17 angle being 180° by symmetry. Linear, rather than bent, coordination of a terminal monodentate dialkyl or alkyl aryl ketone ligand is unusual, particularly in compounds where a significant degree of *d*-orbital metal–ligand covalency might be expected (Fig. 2). The five previous examples with an $\text{Fe}-\text{O}=\text{CR}_2$ angle greater than 170° (Fig. 2) in *d*-block chemistry involve d^0 Zr^{IV} (Sun *et al.*, 1997) or d^{10} Cu^I (Munakata *et al.*, 1994) and Hg^{II} (Lee *et al.*, 2001) metal ions, or weak apical or axial interactions to tetragonal copper(II) centres (Scott & Holm, 1994; Akitsu &

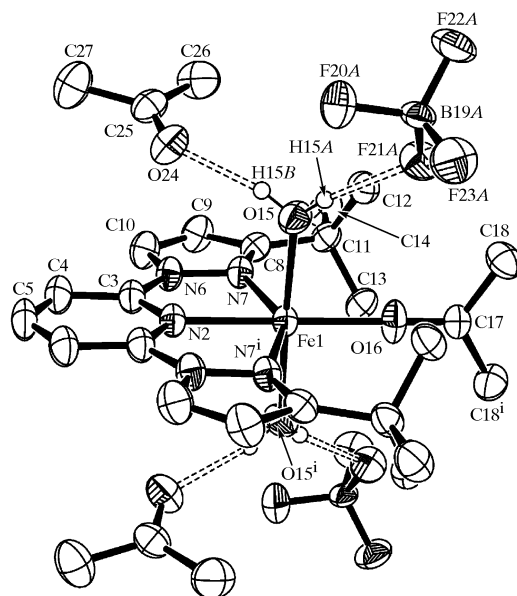


Figure 1

The molecular structure of the components of (I), showing the atom-numbering scheme employed. All C-bound H atoms, and the minor anion disorder orientation (B19B/F20B–F23B) have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level, except for H atoms, which have arbitrary radii. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$]

Einaga, 2004). Of particular relevance is *trans*-[RhCl₂-(Phebox)(OCMe₂)] [HPhebox is 1,3-bis(4-methyloxazolin-2-yl)benzene], which is isoelectronic with and stereochemically similar to (I) but contains a bent acetone ligand with an Rh—O=C angle of 137 (1)° (Motoyama *et al.*, 2001).

The linear Fe1—O16—C17 angle in (I) is probably sterically imposed by the surrounding *tert*-butyl groups (Fig. 3), since atom O16 is in close contact with one H atom from each of the C12 and C13 methyl groups, with C12···O16 = 3.528 (3) Å and C13···O16 = 3.362 (3) Å. For comparison, the sum of the van der Waals radii of an O atom and a methyl group is 3.4 Å (Pauling, 1960). This steric influence is also probably why the

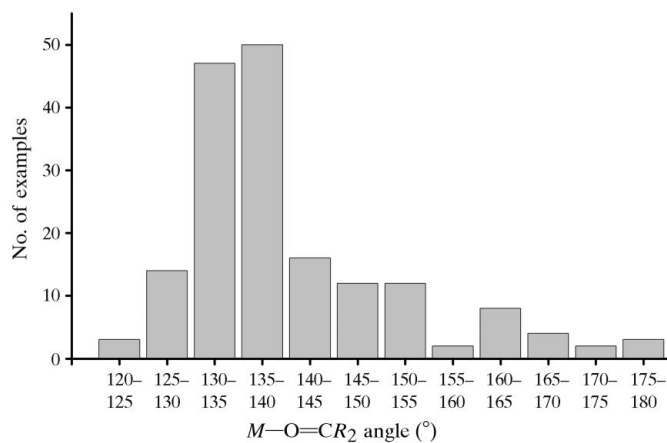


Figure 2
The distribution of $M-O=CR_2$ angles in *d*- and *f*-block metal complexes of acetone, and other monodentate dialkyl and alkyl aryl ketones in the Cambridge Structural Database (July 2006 Version; Allen, 2002).

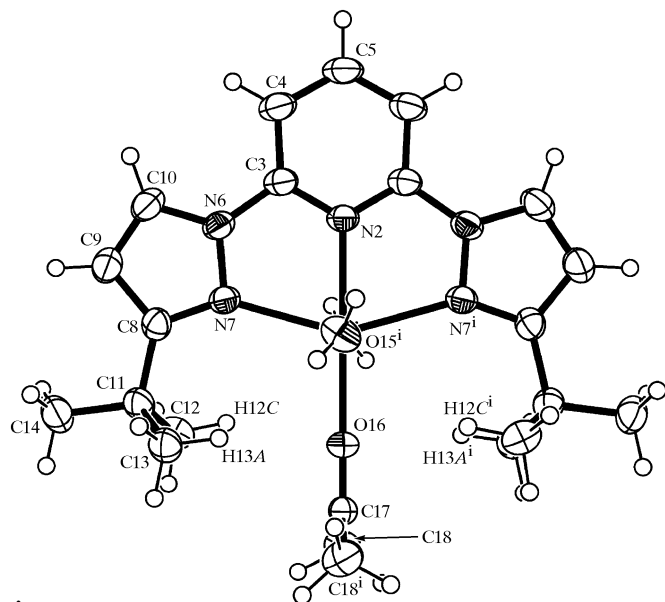


Figure 3
An alternative view of the complex dication in (I), showing the close approach of the *tert*-butyl methyl groups to the coordinated acetone ligand. Displacement ellipsoids are at the 50% probability level, except for H atoms, which have arbitrary radii. The view is approximately parallel to the O15—Fe1—O15ⁱ vector, with Fe1 and O15 hidden behind O15ⁱ. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$].

Fe1—N7 bond is 0.07–0.10 Å longer than we have previously observed in high-spin complexes of 2,6-dipyrazolylpyridines with regular six-coordinate structures (Halcrow, 2005, and references therein). In contrast, the Fe1—O16 bond length is somewhat shorter than those in the only other two known high-spin iron(II) acetone complexes, which have Fe—O distances of 2.113 (2) [Fe—O=CMe₂ = 134.91 (18)°] and 2.123 (2) Å [135.9 (2)°] (Costes *et al.*, 2002). Unfortunately, this sample is too small to determine whether a meaningful correlation exists between the Fe—O distance and Fe—O=C angle in these complexes. One more iron(II) acetone complex is known (Hamon *et al.*, 1994), but since it contains an intermediate-spin iron centre it is not strictly comparable with (I).

The O15 water ligand hydrogen bonds to one F atom of the disordered BF₄[−] anion in the asymmetric unit of (I) through H15A, and to the acetone solvent molecule through H15B (Fig. 1 and Table 2). Therefore, (I) exists as discrete [FeL-(OH₂)₂(OCMe₂)](BF₄)₂·2Me₂CO supramolecules, which associate with each other through van der Waals contacts only.

Experimental

A solution of *L* (0.25 g, 7.7×10^{-4} mol) (Jameson & Goldsby, 1990) and Fe(BF₄)₂·6H₂O (0.13 g, 3.9×10^{-4} mol) in acetone (30 ml) was stirred at room temperature in air until all the solid had dissolved. The colourless solution was concentrated *in vacuo* to ca 5 ml and filtered. Slow diffusion of diethyl ether vapour into the solution yielded colourless crystals of (I) (yield 0.19 g, 64%). The crystals decompose to a very pale-green powder following exposure to air for a period of minutes. Analysis of the dried material implied that all the acetone solvent had been lost and about half of the coordinated acetone in the solid had been replaced with water from atmospheric moisture. The stoichiometry of acetone in the final product was confirmed by IR analysis and by the acetone methyl ¹H NMR peak listed below, which only integrates to ca 3.5H relative to the other peaks in the spectrum [the complex molecule in crystalline (I) would give an acetone peak integrating to 6H]. Analysis found: C 38.7, H 5.1, N 10.9%; calculated for [Fe(C₁₉H₂₅N₅)(C₃H₆O)_{0.5}(H₂O)_{2.5}](BF₄)₂: C 39.3, H 5.3, N 11.2%. IR (nujol): 3425 (*br*, ν O—H), 1692 (*m*, ν C=O), 1642 (*br*, δ H—O—H), 1070 (*vs*, ν B—F) cm^{−1}. ¹H NMR (250.1 MHz, CD₃NO₂, 293 K): δ 69.0, 65.0, 31.9 (all 2H, py H^{3/5} + *pz* H⁴ and H⁵), 2.0 [3.5H, (CH₃)₂CO], −0.2 [18H, C(CH₃)₃], −2.9 (1H, py H⁴).

Crystal data

[Fe(C₁₉H₂₅N₅)(C₃H₆O)-(H₂O)₂](BF₄)₂·2C₃H₆O
 $M_r = 763.18$
 Monoclinic, $C2/c$
 $a = 24.4575$ (4) Å
 $b = 12.7827$ (1) Å
 $c = 14.5598$ (4) Å
 $\beta = 126.323$ (1)°

$V = 3667.40$ (12) Å³
 $Z = 4$
 $D_x = 1.382$ Mg m^{−3}
 Mo $K\alpha$ radiation
 $\mu = 0.49$ mm^{−1}
 $T = 150$ (2) K
 Rectangular prism, colourless
 $0.46 \times 0.33 \times 0.26$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω and φ scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.745$, $T_{\max} = 0.981$
 (expected range = 0.668–0.879)

36356 measured reflections
 4190 independent reflections
 3718 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.131$
 $\theta_{\text{max}} = 27.5^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 2.6971P]$
$R[F^2 > 2\sigma(F^2)] = 0.046$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\max} < 0.001$
$S = 1.04$	$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
4190 reflections	$\Delta\rho_{\min} = -0.68 \text{ e } \text{\AA}^{-3}$
259 parameters	Extinction correction: <i>SHELXL97</i>
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0057 (7)

Table 1

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

Fe1—N2	2.112 (2)	Fe1—O15	2.0857 (14)
Fe1—N7	2.2739 (15)	Fe1—O16	2.0676 (17)
N2—Fe1—N7	74.50 (4)	N7—Fe1—O15 ⁱ	91.31 (6)
N2—Fe1—O15	91.35 (4)	N7—Fe1—O16	105.50 (4)
N2—Fe1—O16	180	O15—Fe1—O15 ⁱ	177.30 (8)
N7—Fe1—N7 ⁱ	149.00 (7)	O15—Fe1—O16	88.65 (4)
N7—Fe1—O15	89.41 (6)		

Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O15—H15A \cdots F21A	0.80 (3)	1.99 (3)	2.771 (3)	164 (3)
O15—H15A \cdots F20B	0.80 (3)	2.01 (3)	2.715 (5)	147 (3)
O15—H15B \cdots O24	0.79 (3)	1.92 (3)	2.689 (2)	165 (3)

The high value of R_{int} is not a consequence of weak high-angle diffraction, since this parameter does not decrease significantly if only low-angle data are merged. Rather, it may be a consequence of the absorption correction applied, or it may simply reflect the high redundancy in the data collection (*ca* nine reflections collected for every unique reflection).

The structure was originally solved and refined in the triclinic space group $P\bar{1}$, with the complex dication lying on a general crystallographic position (*i.e.* $Z = 2$). However, a check for higher symmetry following this initial refinement, using the ADDSYM routine in *PLATON* (Spek, 2003), suggested that the higher-symmetry space group $C2/c$ might be more appropriate. The data were transformed into $C2/c$ and the structure was then solved again and refined, leading to the final model described here.

The asymmetric unit contains half a complex dication, lying on the crystallographic C_2 axis $[0, y, \frac{1}{4}]$, which passes through atoms Fe1, N2, C5, H5, O16 and C17, and one BF_4^- anion and an acetone solvent molecule lying on general positions. The BF_4^- ion B19/F20—F23 is disordered over two orientations, labelled *A* (refined occupancy 0.65) and *B* (0.35). All B—F bonds were restrained to 1.38 (2) \AA during refinement, and all $F\cdots F$ distances within a given disorder orientation to 2.25 (2) \AA . All non-H atoms, except for the minor anion

disorder site, were refined anisotropically. All C-bound H atoms were placed in calculated positions and refined using a riding model with the methyl group torsion angles allowed to refine freely [C—H = 0.95 \AA and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aryl, and C—H = 0.98 \AA and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms]. The water H atoms H15A and H15B were located in a difference map and allowed to refine freely with a common U_{iso} parameter, which refined to 0.063 (6) \AA^2 . The refined O15—H distances are 0.79 (3) and 0.80 (3) \AA , while the H15A—O15—H15B angle is 105 (3) $^\circ$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG3033). Services for accessing these data are described at the back of the journal.

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Computing details

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diaqua(diethyl ether)[2,6-bis(3-*tert*-butylpyrazol-1-yl)pyridine]iron(II) bis(tetrafluoroborate) diethyl ether disolvate

Crystal data

[Fe(C₁₉H₂₅N₅)(C₃H₆O)(H₂O)₂](BF₄)₂·2C₃H₆O

$M_r = 763.18$

Monoclinic C2/c

Hall symbol: -C 2yc

$a = 24.4575$ (4) Å

$b = 12.7827$ (1) Å

$c = 14.5598$ (4) Å

$\beta = 126.323$ (1)°

$V = 3667.40$ (12) Å³

$Z = 4$

$F(000) = 1592$

$D_x = 1.382$ Mg m⁻³

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

Cell parameters from 36356 reflections

$\theta = 2.8$ – 27.5 °

$\mu = 0.49$ mm⁻¹

$T = 150$ K

Rectangular prism, colourless

$0.46 \times 0.33 \times 0.26$ mm

Data collection

Nonius KappaCCD area-detector diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9.091 pixels mm⁻¹

ω and ϕ scans

Absorption correction: multi-scan

Using multiple and symmetry-related data measurements via the program *SORTAV* See

R.H. Blessing (1995), *Acta Cryst.* A51, 33–38

$T_{\min} = 0.745$, $T_{\max} = 0.981$

36356 measured reflections

4190 independent reflections

3718 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.131$

$\theta_{\max} = 27.5$ °, $\theta_{\min} = 2.8$ °

$h = -31 \rightarrow 31$

$k = -16 \rightarrow 16$

$l = -18 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.125$

$S = 1.04$

4190 reflections

259 parameters

20 restraints

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.062P)^2 + 2.6971P]$$

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

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

$$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.68 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL97*,

$$F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$$

Extinction coefficient: 0.0057 (7)

Special details

Experimental. Detector set at 30 mm from sample with different 2theta offsets 1 degree phi exposures for chi=0 degree settings 1 degree omega exposures for chi=90 degree settings

The high value of R_{int} reflects the very high redundancy in the data collection (ca 9 reflections collected for every 1 unique).

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. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

The structure was originally solved and refined in the triclinic space group P-1, with the complex dication lying on a general crystallographic position (i.e. $Z = 2$). However, a check for higher symmetry following this initial refinement using the ADSYMM routine in *PLATON* (Spek, 2003) suggested that the higher symmetry space group $C2/c$ might be more appropriate. The data were transformed into $C2/c$ and the structure was then re-solved and refined, leading to the final model described here.

The asymmetric unit contains half a complex dication, lying on the crystallographic C_2 axis $[0, y, 1/4]$, which passes through Fe1, N2, C5, H5, O16 and C17, and one BF_4^- anion and acetone solvent molecule lying on general positions. The BF_4^- ion is disordered over two orientations, labelled 'A' (refined occupancy 0.65) and 'B' (0.35). All B—F bonds were restrained to 1.38 Å during refinement, and all $F \cdots F$ distances within a given disorder orientation to 2.25 (2) Å. All non-H atoms except for the minor anion disorder site were refined anisotropically. All C-bound H atoms were placed in calculated positions and refined using a riding model with the methyl group torsions allowed to refine freely. The water H atoms were located in the difference map, and allowed to refine freely with a common U_{eq} thermal parameter. The refined O15—H distances are 0.79 (3) and 0.80 (3) Å, while the H15A—O15—H15B angle is 105 (3)°.

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	0.0000	0.30658 (2)	0.2500	0.02901 (14)	
N2	0.0000	0.47179 (15)	0.2500	0.0323 (4)	
C3	0.02961 (9)	0.52457 (13)	0.21176 (14)	0.0346 (4)	
C4	0.03140 (10)	0.63327 (14)	0.20994 (17)	0.0431 (4)	
H4	0.0531	0.6695	0.1826	0.052*	
C5	0.0000	0.68583 (19)	0.2500	0.0467 (7)	
H5	0.0000	0.7601	0.2500	0.056*	
N6	0.05990 (8)	0.46157 (11)	0.17439 (13)	0.0355 (3)	
N7	0.06095 (7)	0.35412 (11)	0.18478 (12)	0.0326 (3)	
C8	0.09541 (9)	0.31925 (14)	0.14600 (15)	0.0340 (4)	
C9	0.11584 (11)	0.40403 (16)	0.11037 (18)	0.0455 (5)	
H9	0.1406	0.4002	0.0791	0.055*	
C10	0.09313 (11)	0.49174 (15)	0.12972 (18)	0.0449 (5)	
H10	0.0992	0.5615	0.1149	0.054*	
C11	0.10866 (9)	0.20394 (14)	0.14358 (16)	0.0363 (4)	

C12	0.14913 (10)	0.15894 (16)	0.26494 (17)	0.0437 (4)	
H12A	0.1943	0.1911	0.3115	0.066*	
H12B	0.1538	0.0831	0.2621	0.066*	
H12C	0.1252	0.1739	0.2986	0.066*	
C13	0.04054 (9)	0.14670 (15)	0.06605 (16)	0.0403 (4)	
H13A	0.0136	0.1568	0.0952	0.060*	
H13B	0.0488	0.0718	0.0649	0.060*	
H13C	0.0157	0.1749	-0.0115	0.060*	
C14	0.14970 (11)	0.18863 (17)	0.0962 (2)	0.0484 (5)	
H14A	0.1246	0.2181	0.0191	0.073*	
H14B	0.1572	0.1138	0.0933	0.073*	
H14C	0.1935	0.2242	0.1456	0.073*	
O15	0.08949 (7)	0.30274 (11)	0.41547 (12)	0.0420 (3)	
H15A	0.1007 (14)	0.267 (2)	0.469 (3)	0.063 (6)*	
H15B	0.1146 (15)	0.351 (2)	0.441 (2)	0.063 (6)*	
O16	0.0000	0.14483 (13)	0.2500	0.0447 (5)	
C17	0.0000	0.04961 (18)	0.2500	0.0322 (5)	
C18	0.05461 (11)	-0.01097 (17)	0.34977 (16)	0.0470 (5)	
H18A	0.0818	-0.0469	0.3302	0.071*	
H18B	0.0344	-0.0627	0.3712	0.071*	
H18C	0.0837	0.0366	0.4139	0.071*	
B19A	0.1530 (4)	0.1692 (5)	0.6886 (5)	0.0332 (14)	0.65
F20A	0.16075 (12)	0.27801 (15)	0.6986 (2)	0.0612 (6)	0.65
F21A	0.12620 (10)	0.14616 (16)	0.57387 (14)	0.0493 (4)	0.65
F22A	0.21371 (10)	0.1205 (2)	0.76035 (19)	0.0547 (6)	0.65
F23A	0.1030 (2)	0.1382 (4)	0.7047 (4)	0.0624 (9)	0.65
B19B	0.1408 (6)	0.1662 (10)	0.6793 (11)	0.037 (4)*	0.35
F20B	0.1244 (2)	0.2604 (3)	0.6267 (4)	0.0604 (10)*	0.35
F21B	0.1284 (2)	0.0865 (4)	0.6080 (4)	0.0618 (10)*	0.35
F22B	0.2102 (4)	0.1638 (5)	0.7691 (6)	0.086 (2)*	0.35
F23B	0.1117 (4)	0.1530 (7)	0.7312 (6)	0.056 (2)*	0.35
O24	0.16066 (8)	0.47987 (12)	0.46096 (14)	0.0504 (4)	
C25	0.20620 (10)	0.50368 (16)	0.45374 (16)	0.0423 (4)	
C26	0.24263 (12)	0.4236 (2)	0.4346 (2)	0.0601 (6)	
H26A	0.2232	0.3544	0.4274	0.090*	
H26B	0.2908	0.4235	0.4992	0.090*	
H26C	0.2379	0.4400	0.3644	0.090*	
C27	0.22717 (14)	0.61492 (19)	0.4639 (2)	0.0624 (6)	
H27A	0.1976	0.6596	0.4717	0.094*	
H27B	0.2235	0.6352	0.3955	0.094*	
H27C	0.2743	0.6231	0.5312	0.094*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.0367 (2)	0.0227 (2)	0.0289 (2)	0.000	0.02004 (16)	0.000
N2	0.0415 (10)	0.0238 (9)	0.0314 (10)	0.000	0.0215 (9)	0.000
C3	0.0431 (9)	0.0262 (8)	0.0324 (8)	-0.0010 (7)	0.0212 (7)	0.0009 (6)

C4	0.0562 (11)	0.0278 (8)	0.0461 (10)	-0.0026 (8)	0.0308 (9)	0.0034 (7)
C5	0.0636 (18)	0.0226 (11)	0.0525 (16)	0.000	0.0337 (15)	0.000
N6	0.0468 (8)	0.0280 (7)	0.0361 (7)	-0.0025 (6)	0.0270 (7)	0.0023 (6)
N7	0.0411 (7)	0.0264 (7)	0.0319 (7)	-0.0021 (6)	0.0225 (6)	-0.0003 (5)
C8	0.0364 (8)	0.0374 (9)	0.0304 (8)	-0.0050 (7)	0.0209 (7)	-0.0047 (6)
C9	0.0569 (11)	0.0441 (10)	0.0511 (11)	-0.0087 (9)	0.0406 (10)	-0.0041 (8)
C10	0.0585 (11)	0.0381 (10)	0.0490 (11)	-0.0066 (8)	0.0378 (10)	0.0039 (8)
C11	0.0371 (9)	0.0365 (9)	0.0379 (9)	-0.0057 (7)	0.0237 (8)	-0.0091 (7)
C12	0.0444 (10)	0.0385 (10)	0.0423 (10)	0.0034 (8)	0.0225 (8)	-0.0035 (8)
C13	0.0417 (9)	0.0408 (10)	0.0417 (10)	-0.0085 (8)	0.0265 (8)	-0.0108 (8)
C14	0.0488 (11)	0.0503 (12)	0.0591 (13)	-0.0105 (9)	0.0392 (10)	-0.0180 (9)
O15	0.0429 (7)	0.0415 (8)	0.0318 (7)	-0.0085 (6)	0.0168 (6)	0.0014 (5)
O16	0.0665 (12)	0.0229 (8)	0.0677 (13)	0.000	0.0523 (11)	0.000
C17	0.0425 (12)	0.0274 (11)	0.0337 (11)	0.000	0.0264 (10)	0.000
C18	0.0538 (11)	0.0454 (11)	0.0348 (9)	0.0091 (9)	0.0223 (9)	0.0031 (8)
B19A	0.026 (2)	0.037 (2)	0.023 (2)	0.0050 (17)	0.0072 (17)	0.0005 (12)
F20A	0.0697 (13)	0.0347 (10)	0.0724 (15)	-0.0012 (9)	0.0383 (12)	-0.0085 (9)
F21A	0.0558 (11)	0.0558 (11)	0.0305 (8)	0.0039 (9)	0.0224 (8)	-0.0028 (8)
F22A	0.0386 (10)	0.0605 (14)	0.0410 (10)	0.0170 (10)	0.0103 (8)	0.0088 (10)
F23A	0.0652 (18)	0.073 (2)	0.0506 (19)	-0.0043 (15)	0.0353 (17)	0.0109 (18)
O24	0.0524 (8)	0.0494 (8)	0.0563 (9)	-0.0147 (6)	0.0360 (7)	-0.0127 (7)
C25	0.0435 (9)	0.0481 (11)	0.0322 (9)	-0.0088 (8)	0.0208 (8)	-0.0073 (7)
C26	0.0542 (12)	0.0686 (15)	0.0563 (13)	0.0015 (11)	0.0320 (11)	-0.0099 (11)
C27	0.0763 (16)	0.0543 (13)	0.0762 (16)	-0.0187 (12)	0.0559 (14)	-0.0118 (12)

Geometric parameters (Å, °)

Fe1—N2	2.112 (2)	C14—H14A	0.9800
Fe1—N7	2.2739 (15)	C14—H14B	0.9800
Fe1—O15	2.0857 (14)	C14—H14C	0.9800
Fe1—O16	2.0676 (17)	O15—H15A	0.80 (3)
N2—C3	1.329 (2)	O15—H15B	0.79 (3)
C3—C4	1.391 (2)	O16—C17	1.217 (3)
C3—N6	1.404 (2)	C17—C18	1.482 (2)
C4—C5	1.383 (2)	C18—H18A	0.9800
C4—H4	0.9500	C18—H18B	0.9800
C5—H5	0.9500	C18—H18C	0.9800
N6—C10	1.363 (2)	B19A—F22A	1.358 (6)
N6—N7	1.3803 (19)	B19A—F20A	1.400 (6)
N7—C8	1.338 (2)	B19A—F21A	1.418 (6)
C8—C9	1.414 (3)	B19A—F23A	1.431 (8)
C8—C11	1.514 (2)	B19B—F23B	1.322 (14)
C9—C10	1.353 (3)	B19B—F21B	1.355 (13)
C9—H9	0.9500	B19B—F20B	1.355 (13)
C10—H10	0.9500	B19B—F22B	1.400 (12)
C11—C14	1.531 (3)	O24—C25	1.218 (2)
C11—C13	1.535 (2)	C25—C26	1.488 (3)
C11—C12	1.536 (3)	C25—C27	1.489 (3)

C12—H12A	0.9800	C26—H26A	0.9800
C12—H12B	0.9800	C26—H26B	0.9800
C12—H12C	0.9800	C26—H26C	0.9800
C13—H13A	0.9800	C27—H27A	0.9800
C13—H13B	0.9800	C27—H27B	0.9800
C13—H13C	0.9800	C27—H27C	0.9800
N2—Fe1—N7	74.50 (4)	C11—C13—H13C	109.5
N2—Fe1—O15	91.35 (4)	H13A—C13—H13C	109.5
N2—Fe1—O16	180	H13B—C13—H13C	109.5
N7—Fe1—N7 ⁱ	149.00 (7)	C11—C14—H14A	109.5
N7—Fe1—O15	89.41 (6)	C11—C14—H14B	109.5
N7—Fe1—O15 ⁱ	91.31 (6)	H14A—C14—H14B	109.5
N7—Fe1—O16	105.50 (4)	C11—C14—H14C	109.5
O15—Fe1—O15 ⁱ	177.30 (8)	H14A—C14—H14C	109.5
O15—Fe1—O16	88.65 (4)	H14B—C14—H14C	109.5
C3 ⁱ —N2—C3	119.0 (2)	Fe1—O15—H15A	131 (2)
C3—N2—Fe1	120.50 (10)	Fe1—O15—H15B	121 (2)
N2—C3—C4	123.10 (18)	H15A—O15—H15B	105 (3)
N2—C3—N6	114.49 (15)	C17—O16—Fe1	180
C4—C3—N6	122.40 (17)	O16—C17—C18	121.51 (12)
C5—C4—C3	116.47 (19)	C18 ⁱ —C17—C18	117.0 (2)
C5—C4—H4	121.8	C17—C18—H18A	109.5
C3—C4—H4	121.8	C17—C18—H18B	109.5
C4—C5—C4 ⁱ	121.9 (2)	H18A—C18—H18B	109.5
C4—C5—H5	119.1	C17—C18—H18C	109.5
C10—N6—N7	110.86 (15)	H18A—C18—H18C	109.5
C10—N6—C3	128.55 (16)	H18B—C18—H18C	109.5
N7—N6—C3	120.54 (14)	F22A—B19A—F20A	110.9 (5)
C8—N7—N6	105.11 (14)	F22A—B19A—F21A	110.1 (4)
C8—N7—Fe1	145.04 (12)	F20A—B19A—F21A	105.6 (4)
N6—N7—Fe1	109.72 (10)	F22A—B19A—F23A	113.5 (5)
N7—C8—C9	110.31 (16)	F20A—B19A—F23A	109.5 (5)
N7—C8—C11	122.06 (16)	F21A—B19A—F23A	107.0 (5)
C9—C8—C11	127.62 (17)	F23B—B19B—F21B	113.0 (10)
C10—C9—C8	106.30 (17)	F23B—B19B—F20B	110.9 (10)
C10—C9—H9	126.8	F21B—B19B—F20B	112.3 (10)
C8—C9—H9	126.8	F23B—B19B—F22B	103.3 (10)
C9—C10—N6	107.41 (17)	F21B—B19B—F22B	107.3 (9)
C9—C10—H10	126.3	F20B—B19B—F22B	109.7 (9)
N6—C10—H10	126.3	O24—C25—C26	121.6 (2)
C8—C11—C14	109.96 (16)	O24—C25—C27	120.6 (2)
C8—C11—C13	109.10 (15)	C26—C25—C27	117.8 (2)
C14—C11—C13	108.86 (15)	C25—C26—H26A	109.5
C8—C11—C12	109.79 (15)	C25—C26—H26B	109.5
C14—C11—C12	108.84 (17)	H26A—C26—H26B	109.5
C13—C11—C12	110.28 (16)	C25—C26—H26C	109.5
C11—C12—H12A	109.5	H26A—C26—H26C	109.5

C11—C12—H12B	109.5	H26B—C26—H26C	109.5
H12A—C12—H12B	109.5	C25—C27—H27A	109.5
C11—C12—H12C	109.5	C25—C27—H27B	109.5
H12A—C12—H12C	109.5	H27A—C27—H27B	109.5
H12B—C12—H12C	109.5	C25—C27—H27C	109.5
C11—C13—H13A	109.5	H27A—C27—H27C	109.5
C11—C13—H13B	109.5	H27B—C27—H27C	109.5
H13A—C13—H13B	109.5		

Symmetry code: (i) $-x, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O15—H15 <i>A</i> \cdots F21 <i>A</i>	0.80 (3)	1.99 (3)	2.771 (3)	164 (3)
O15—H15 <i>A</i> \cdots F20 <i>B</i>	0.80 (3)	2.01 (3)	2.715 (5)	147 (3)
O15—H15 <i>B</i> \cdots O24	0.79 (3)	1.92 (3)	2.689 (2)	165 (3)