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*-butyl-pyrazol-1-yl)pyridine]iron(II) bis(tetrafluoroborate) acetone disolvate, $[Fe(C_{19}H_{25}N_5)(C_3H_6O)(H_2O)_2](BF_4)_2·2C_3H_6O$, contains a C_2-symmetric six-coordinate complex dication, with an acetone ligand in its equatorial plane that is linearly coordinated by symmetry (Fe—O=CMe$_2$ = 180°). 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-dipyrazolyl-pyrazine 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; Elhaïk *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 [Fe*L*$_2$]$^{2+}$ centre. In fact, as we had already observed in its copper chemistry (Solanki *et al.*, 2002), *L* proved too bulky to allow [Fe*L*$_2$]$^{2+}$ to form. Hence, when hydrated Fe(BF$_4$)$_2$ and two molar equivalents of *L* were reacted in MeOH, MeCN or MeNO$_2$, the resulting yellow solutions only yielded single crystals of unreacted *L* (Halcrow, 2005) and/or small amounts of intractable powder when layered with Et$_2$O. A pure iron-containing product was only obtained when these reactions were performed in acetone, giving near-colourless crystals of *trans*-[Fe*L*(OH$_2$)$_2$(OCMe$_2$)](BF$_4$)$_2$·2Me$_2$CO, (I). This compound was obtained in pure form when Fe(BF$_4$)$_2$·6H$_2$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

(I)
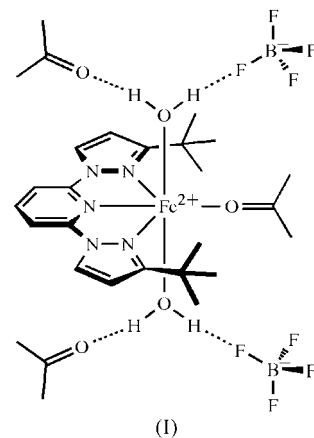
74.50 (4)° bite angle of the *L* ligand (Table 1). The metal coordination is completed by an acetone ligand occupying the fourth equatorial coordination site and by two axial water ligands. Notably, the acetone ligand is coordinated in a linear fashion, the Fe1—O16—C17 angle being 180° by symmetry. Linear, rather than bent, coordination of a terminal mono-dentate dialkyl or alkyl aryl ketone ligand is unusual, parti-cularly in compounds where a significant degree of *d*-orbital metal–ligand covalency might be expected (Fig. 2). The five previous examples with an Fe—O=C*R*$_2$ 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 &
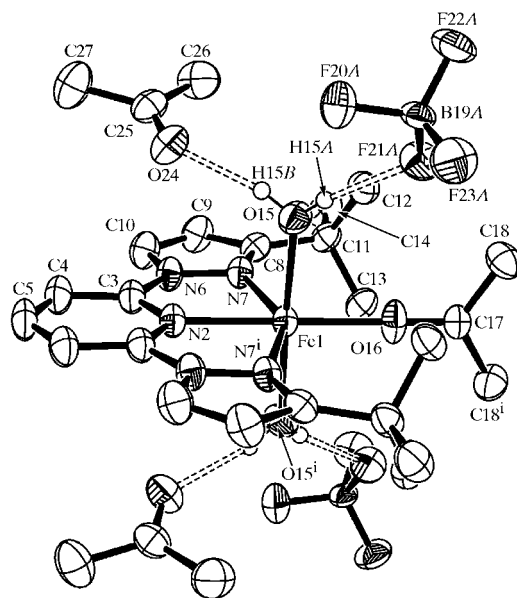

Figure 1
The molecular structure of the components of (I), showing the atom-numbering scheme employed. All C-bound H atoms, and the minor anion disorder orientation (B19*B*/F20*B*–F23*B*) have been omitted for clarity. Displacement ellipsoids are shown at the 50% probability level, except for H atoms, which have arbitrary radii. [Symmetry code: (i) $-x, y, -z + \frac{1}{2}$.]

Einaga, 2004). Of particular relevance is *trans*-[RhCl$_2$-(Phebox)(OCMe$_2$)] [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
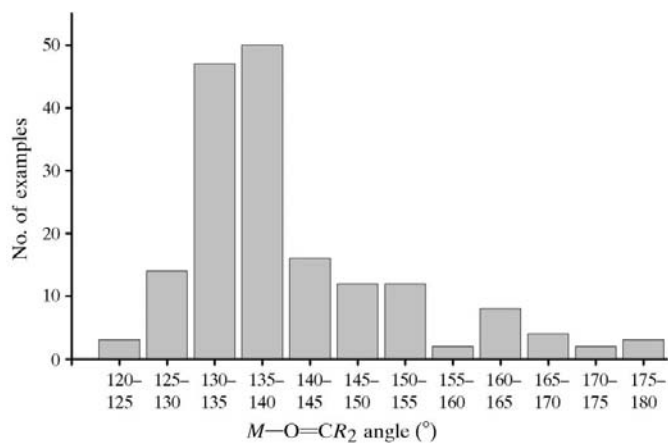

Figure 2
The distribution of M—O=CR_2 angles in *d*- and *f*-block metal complexes of acetone, and other monodentate dialkyl and alkyl aryl ketones in the Cambridge Structural Database (July 2006 Version; Allen, 2002).
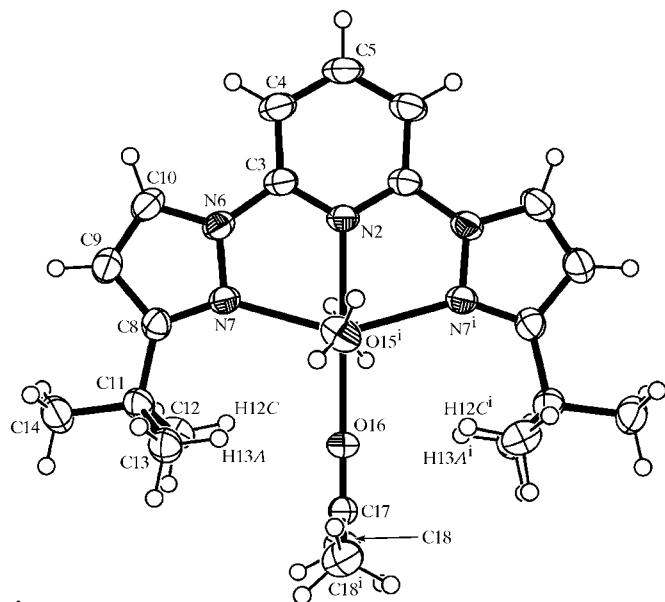

Figure 3
An alternative view of the complex dication in (I), showing the close approach of the *tert*-butyl methyl groups to the coordinated acetone ligand. Displacement ellipsoids are at the 50% probability level, except for H atoms, which have arbitrary radii. The view is approximately parallel to the O15—Fe1—O15^i vector, with Fe1 and O15 hidden behind O15^i. [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=CMe$_2$ = 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=CR_2 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 BF$_4^-$ anion in the asymmetric unit of (I) through H15*A*, and to the acetone solvent molecule through H15*B* (Fig. 1 and Table 2). Therefore, (I) exists as discrete [Fe*L*-(OH$_2$)$_2$(OCMe$_2$)](BF$_4$)$_2$·2Me$_2$CO 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(BF$_4$)$_2$·6H$_2$O (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 ^{1}H 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(C$_{19}$H$_{25}$N$_5$)(C$_3$H$_6$O)$_{0.5}$(H$_2$O)$_{2.5}$]-(BF$_4$)$_2$: 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}. ^{1}H NMR (250.1 MHz, CD$_3$NO$_2$, 293 K): δ 69.0, 65.0, 31.9 (all 2H, py H$^{3/5}$ + pz H^4 and H^5), 2.0 [3.5H, (CH$_3$)$_2$CO], −0.2 [18H, C(CH$_3$)$_3$], −2.9 (1H, py H^4).

Crystal data

[Fe(C$_{19}$H$_{25}$N$_5$)(C$_3$H$_6$O)-(H$_2$O)$_2$](BF$_4$)$_2$·2C$_3$H$_6$O	$V = 3667.40$ (12) Å^3
$M_r = 763.18$	$Z = 4$
Monoclinic, $C2/c$	$D_x = 1.382$ Mg m^{-3}
$a = 24.4575$ (4) Å	Mo $K\alpha$ radiation
$b = 12.7827$ (1) Å	$\mu = 0.49$ mm^{-1}
$c = 14.5598$ (4) Å	$T = 150$ (2) K
$\beta = 126.323$ (1)°	Rectangular prism, colourless
	$0.46 \times 0.33 \times 0.26$ mm

Data collection

Nonius KappaCCD area-detector diffractometer	36356 measured reflections
ω and φ scans	4190 independent reflections
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	3718 reflections with $I > 2\sigma(I)$
$T_{min} = 0.745$, $T_{max} = 0.981$	$R_{int} = 0.131$
(expected range = 0.668–0.879)	$\theta_{max} = 27.5$°

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 $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.04$	$\Delta\rho_{max} = 0.45$ e Å^{-3}
4190 reflections	$\Delta\rho_{min} = -0.68$ e Å^{-3}
259 parameters	Extinction correction: *SHELXL97*
H atoms treated by a mixture of independent and constrained refinement	Extinction coefficient: 0.0057 (7)

Table 1
Selected geometric parameters (Å, °).

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 (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O15—H15A···F21A	0.80 (3)	1.99 (3)	2.771 (3)	164 (3)
O15—H15A···F20B	0.80 (3)	2.01 (3)	2.715 (5)	147 (3)
O15—H15B···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) Å during refinement, and all F···F distances within a given disorder orientation to 2.25 (2) Å. All non-H atoms, except for the minor anion

disorder site, were refine 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 Å and U_{iso}(H) = 1.2U_{eq}(C) for aryl, and C—H = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(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) Å^2. The refined O15—H distances are 0.79 (3) and 0.80 (3) Å, while the H15A—O15—H15B angle is 105 (3)°.

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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