

{Tris[4-(1*H*-pyrazol-3-yl)-3-azabut-3-enyl]amine}iron(II) diperchlorate monohydrate

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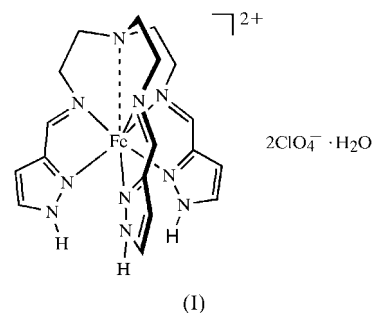
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In the title complex, $[\text{Fe}(\text{C}_{18}\text{H}_{24}\text{N}_{10})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, the complex cation adopts a capped trigonal antiprismatic stereochemistry, with a long Fe–amine interaction [2.7468 (16) Å]. The Fe centre in the asymmetric unit is fully high-spin at 100 K. Hydrogen bonding assembles dimeric units, which are then linked by further hydrogen bonding into chains running parallel to the crystallographic *a* axis.

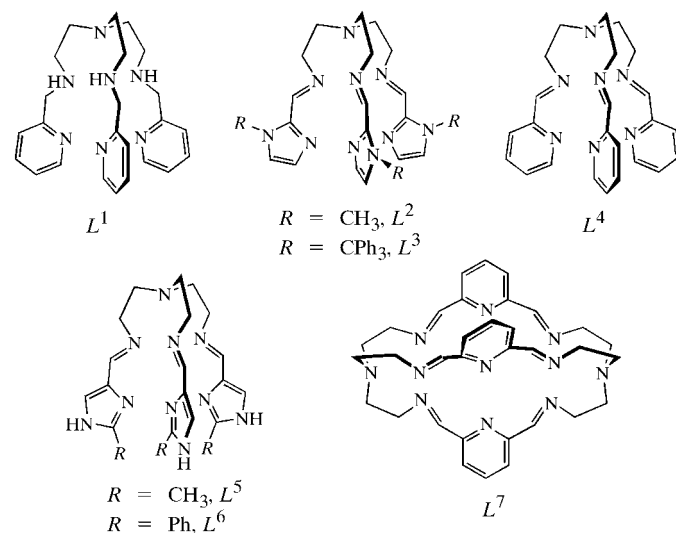
Comment

We have been interested for some time in the spin-state transitions shown by iron(II) complexes of polydentate pyrazole-containing ligands (Holland *et al.*, 2001; Holland, Barrett *et al.*, 2002; Holland, McAllister *et al.*, 2002; Elhaik *et al.*, 2003; Money *et al.*, 2003, 2004; Smithson *et al.*, 2003). During this work, we noted that both iron(II) and iron(III) complexes of tris[4-(imidazol-2-yl)-3-aza-3-butenyl]amine, the Schiff base derived from the reaction of tris(2-aminoethyl)amine (tren) with three equivalents of imidazole-2-carbaldehyde, and closely related derivatives exhibit interesting spin-state transitions (Nagasato *et al.*, 2001; Sunatsuki *et al.*, 2001; Ikuta *et al.*, 2003; Yamada *et al.*, 2003; Yukinari *et al.*, 2003). We therefore decided to investigate the iron chemistry of the pyrazole-containing analogue tris[4-(1*H*-pyrazol-3-yl)-3-aza-3-butenyl]amine. We found that reactions of this ligand with hydrated $\text{Fe}(\text{ClO}_4)_3$ in MeOH yielded a dark-brown precipitate. Some of this material proved soluble on extraction with acetone, giving a dark-orange solution that afforded orange crystals of the title compound, (I), following diffusion of diethyl ether vapour into the mixture. Presumably, partial reduction of the Fe^{III} content of the mixture by the MeOH solvent took place during the reaction. Compound (I) was subsequently synthesized in higher yield by direct treatment of the same ligand with $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. No complexes of tris[4-(1*H*-pyrazol-3-yl)-3-aza-3-butenyl]amine have been reported before, although Ni^{II} and Co^{III} complexes of its trimethylated

derivative, tris[4-(5-methyl-1*H*-pyrazol-3-yl)-3-aza-3-butenyl]amine, have been structurally characterized (Paul *et al.*, 2000, 2002).



The coordination geometry about the Fe centre in (I) (Fig. 1) is best described as a capped trigonal antiprism. There are six Fe–N bonds of 2.1563 (16)–2.2547 (16) Å (Table 1) to the imine and pyrazole N-atoms donors, these lengths being typical of a high-spin Fe^{II} centre. Amine atom N2 lies at a much longer distance [2.7468 (16) Å] from the metal atom, at a position approximately central above the triangular face formed by atoms N5, N14 and N23. This distance is at the lower end of the range of capping Fe–N distances seen for high-spin Fe^{II} complexes of related heptadentate tripodal ligands. As can be seen from Table 3, there is an approximate positive correlation in this class of compound (for the ligands shown in the scheme below) between contraction of this capping Fe–N bond and an opening out of the capped face of the trigonal antiprism, indicated by an increase in the $\text{N}_{\text{imine}}-\text{Fe}-\text{N}_{\text{imine}}$ angles [N5–Fe1–N14, N5–Fe1–N23 and N14–Fe1–N23 in (I)]. However, there is no apparent relation between these structural parameters and whether or not these compounds undergo spin-crossover upon cooling. Although the helical ligand conformation about each Fe atom is chiral, (I) crystallizes as a racemate in the centrosymmetric space group $P2_1/n$.



Two of the three pyrazole NH groups in (I) are hydrogen bonded to two different lattice water molecules, forming $\text{N9}-\text{H9} \cdots \text{O40}$ and $\text{N18}-\text{H18} \cdots \text{O40}^{\text{i}}$ interactions [symmetry

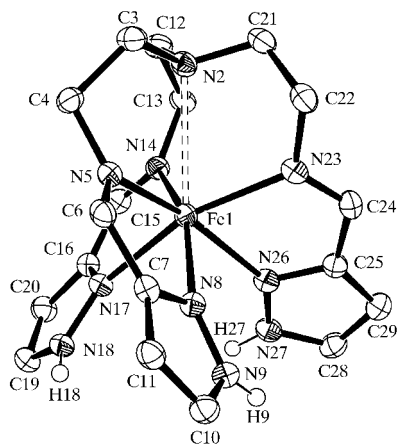


Figure 1
The molecular structure of the complex cation in the crystal structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. All C-bound H atoms have been omitted for clarity.

code: (i) $1 - x, 1 - y, 1 - z$; Table 2]. The third NH group (N27–H27) hydrogen bonds to atom O31 in one of the two independent ClO_4^- anions. This same anion accepts a hydrogen bond from water atom H40Aⁱⁱ [symmetry code: (ii) $x - 1, y, z$]. The other water H atom (H40B) hydrogen bonds to the other ClO_4^- ion in the asymmetric unit. The net effect of these interactions is to assemble two formula units into a hydrogen-bonded dimer about the inversion centre at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (Fig. 2). These dimers are in turn linked into chains running

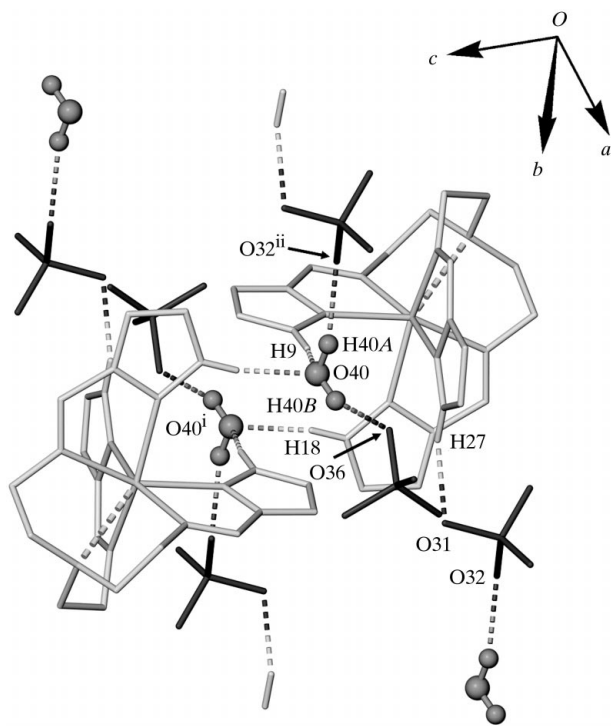


Figure 2
A partial packing diagram of (I), showing the centrosymmetric hydrogen-bonded dimerization of the formula units in the structure. [Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x - 1, y, z$].

parallel to the crystallographic a direction through the Cl30/O34 anion, which accepts hydrogen bonds from two different dimer moieties.

Experimental

A solution of the tris[4-(1*H*-pyrazol-3-yl)-3-aza-3-butenyl]amine ligand was prepared by refluxing a mixture of pyrazole-3-carbaldehyde (1.00 g, 10.4 mmol) and tris(2-aminoethyl)amine (0.51 g, 3.47 mmol) in MeOH (100 ml) until all of the solid had dissolved. $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (1.26 g, 3.47 mmol) was then added to the mixture, yielding a dark-yellow solution. The volume was reduced to ~ 10 ml by evaporation, and then an excess of diethyl ether was added to yield a yellow–orange precipitate (yield 1.23 g, 56%). Recrystallization of the crude product from undried acetone gave orange monohydrated crystals, which lost their water of crystallization upon drying *in vacuo* over P_2O_5 . Analysis found: C 34.0, H 3.9, N 22.2%; calculated for $\text{C}_{18}\text{H}_{24}\text{Cl}_2\text{FeN}_{10}\text{O}_8$: C 34.0, H 3.8, N 22.1%.

Crystal data

$[\text{Fe}(\text{C}_{18}\text{H}_{24}\text{N}_{10})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$
 $M_r = 653.24$
 Monoclinic, $P2_1/n$
 $a = 9.4086$ (1) Å
 $b = 22.5317$ (4) Å
 $c = 12.7279$ (2) Å
 $\beta = 101.9858$ (6)°
 $V = 2639.38$ (7) Å³
 $Z = 4$

$D_x = 1.644$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 25 327 reflections
 $\theta = 1.8$ – 27.5°
 $\mu = 0.84$ mm⁻¹
 $T = 100$ (2) K
 Rectangular prism, orange
 $0.33 \times 0.23 \times 0.20$ mm

Data collection

Nonius KappaCCD area-detector diffractometer
 ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.769, T_{\max} = 0.850$
 25 327 measured reflections

6004 independent reflections
 4724 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.066$
 $\theta_{\max} = 27.5^\circ$
 $h = -12 \rightarrow 12$
 $k = -29 \rightarrow 29$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.099$
 $S = 1.04$
 6004 reflections
 370 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 1.086P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.34 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.51 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Fe1–N2	2.7468 (17)	Fe1–N17	2.2413 (17)
Fe1–N5	2.1563 (16)	Fe1–N23	2.1628 (17)
Fe1–N8	2.2547 (16)	Fe1–N26	2.2457 (16)
Fe1–N14	2.1575 (17)		
N2–Fe1–N5	67.23 (5)	N8–Fe1–N14	159.82 (6)
N2–Fe1–N8	128.69 (5)	N8–Fe1–N17	86.13 (6)
N2–Fe1–N14	68.49 (6)	N8–Fe1–N23	91.34 (6)
N2–Fe1–N17	126.82 (6)	N8–Fe1–N26	87.25 (6)
N2–Fe1–N23	68.08 (6)	N14–Fe1–N17	73.95 (6)
N2–Fe1–N26	126.16 (5)	N14–Fe1–N23	106.51 (6)
N5–Fe1–N8	74.02 (6)	N14–Fe1–N26	88.90 (6)
N5–Fe1–N14	109.45 (6)	N17–Fe1–N23	161.53 (7)
N5–Fe1–N17	92.64 (6)	N17–Fe1–N26	88.21 (6)
N5–Fe1–N23	104.25 (6)	N23–Fe1–N26	73.39 (6)
N5–Fe1–N26	161.14 (6)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N9—H9 \cdots O40	0.88	2.00	2.848 (2)	160
N18—H18 \cdots O40 ⁱ	0.88	1.97	2.833 (2)	168
N27—H27 \cdots O31	0.88	2.03	2.848 (2)	155
O40—H40A \cdots O32 ⁱⁱ	0.854 (19)	2.04 (2)	2.728 (2)	137.1 (16)
O40—H40B \cdots O36	0.84 (2)	2.07 (2)	2.832 (2)	149 (2)

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-1, y, z$.**Table 3**Selected structural parameters for high-spin Fe^{II} complexes of the ligands shown the second scheme in the *Comment*.

a is the distance between the Fe and bridgehead N atoms [Fe1—N2 in (I)], θ is the average of the three $N_{\text{imine}}-\text{Fe}-N_{\text{imine}}$ angles, and ω is the average of the three $N_{\text{heterocycle}}-\text{Fe}-N_{\text{heterocycle}}$ angles.

Compound	a (Å)	θ (°)	ω (°)	Spin-crossover on cooling
[Fe(L^1)](ClO ₄) ₂ [†]	2.504 (6)	112.7 (2)	86.1 (2)	No
[Fe(L^2)](PF ₆) ₂ [‡]	2.724 (4)	106.6 (3)	86.6 (3)	N/a
(I) [§]	2.7468 (16)	106.73 (10)	87.20 (10)	N/a
[Fe(L^4)](PF ₆) ₂ [†]	2.753 (8)	N/a	N/a	Yes
[Fe(L^3)](PF ₆) ₂ [¶]	3.004 (8)	100.2 (7)	98.0 (6)	No
[[Fe(L^5) ₂ H ₃]NO ₃] ^{††}	3.122 (6)	97.93 (13)	93.13 (13)	Yes
	3.169 (9)	98.30 (12)	92.95 (12)	Yes
[[Fe(L^5) ₂ H ₃]PF ₆] ^{‡‡}	3.198 (8)	97.14 (13)	94.41 (13)	Yes
	3.215 (8)	97.18 (14)	94.47 (13)	Yes
[Fe(L^6)](PF ₆) ₂ ^{§§}	3.261 (5)	96.5 (3)	97.7 (5)	No
[Fe(L^7)](ClO ₄) ₂ ^{¶¶}	3.280 (3)	91.5 (2)	102.1 (2)	No

[†] Morgenstern-Badarau *et al.* (2000). [‡] Yang *et al.* (2001). [§] This work; the compound does not undergo spin-crossover above 100 K. [¶] Morgenstern-Badarau *et al.* (1998). ^{††} Ikuta *et al.* (2003). ^{‡‡} Yamada *et al.* (2003). ^{§§} Nagasato *et al.* (2001). ^{¶¶} Deeney *et al.* (1998).

The data set used for the refinement is 99.3% complete to $2\theta = 50^\circ$. All H atoms in the complex dication were placed in calculated positions and treated using a riding model, with Csp^2-H distances of 0.95 Å, Csp^3-H distances of 0.99 Å and N—H distances of 0.88 Å, and all $U_{\text{iso}}(\text{H})$ parameters were fixed at $1.2U_{\text{eq}}(\text{C}, \text{N})$. Water atoms H40A and H40B were located in a difference map and included in the refinement with O—H distances restrained to 0.84 (1) Å and H \cdots H distances restrained to 1.37 (1) Å. An antibumping restraint was also applied between atoms H9 and H40A. In the refined water molecule, the O40—H40A distance is 0.854 (19) Å, the O40—H40B distance is 0.84 (2) Å and the H40A—O40—H40B angle is 106.0 (15)°.

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: BM1561). Services for accessing these data are described at the back of the journal.

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