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

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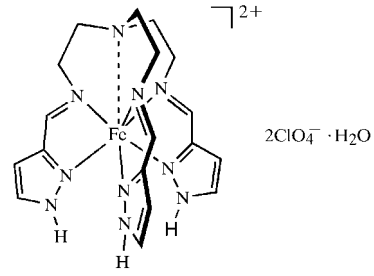
In the title complex, $[Fe(C_{18}H_{24}N_{10})](ClO_4)_2\cdot H_2O$, the complex cation adopts a capped trigonal antiprismatic stereochemistry, with a long Fe–amine interaction [2.7468 (16) Å]. The Fe centre in the asymmetric unit is fully high-spin at 100 K. Hydrogen bonding assembles dimeric units, which are then linked by further hydrogen bonding into chains running parallel to the crystallographic *a* axis.

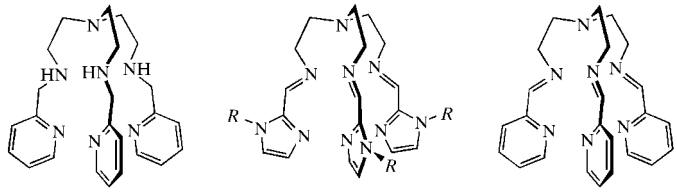
Comment

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; Elhaïk *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 $Fe(ClO_4)_3$ 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 $Fe(ClO_4)_2\cdot 6H_2O$. 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).

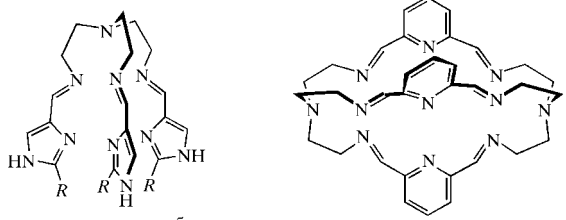


(I)

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 N_{imine}—Fe—N_{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 $P2_1/n$.



L^1 $R = CH_3$, L^2 $R = CPh_3$, L^3 L^4



$R = CH_3$, L^5 $R = Ph$, L^6 L^7

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

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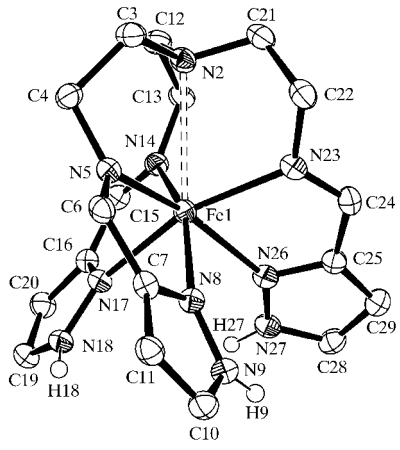

Figure 1
The molecular structure of the complex cation in the crystal structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. All C-bound H atoms have been omitted for clarity.

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 H40*A*^{ii} [symmetry code: (ii) $x-1, y, z$]. The other water H atom (H40*B*) 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 parallel to the crystallographic *a* direction through the Cl30/O34 anion, which accepts hydrogen bonds from two different dimer moieties.

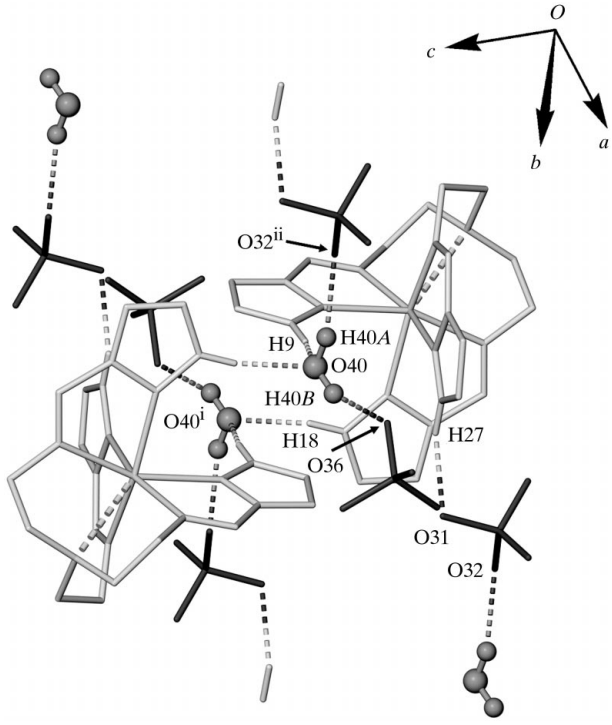

Figure 2
A partial packing diagram of (I), showing the centrosymmetric hydrogen-bonded dimerization of the formula units in the structure. [Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $x-1, y, z$.]

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. $Fe(ClO_4)_2\cdot 6H_2O$ (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 $C_{18}H_{24}Cl_2FeN_{10}O_8$: C 34.0, H 3.8, N 22.1%.

Crystal data

$[Fe(C_{18}H_{24}N_{10})](ClO_4)_2\cdot H_2O$	$D_x = 1.644$ Mg m^{-3}
$M_r = 653.24$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25 327 reflections
$a = 9.4086$ (1) Å	$\theta = 1.8$–$27.5°$
$b = 22.5317$ (4) Å	$\mu = 0.84$ mm^{-1}
$c = 12.7279$ (2) Å	$T = 100$ (2) K
$\beta = 101.9858$ (6)°	Rectangular prism, orange
$V = 2639.38$ (7) Å^3	0.33 × 0.23 × 0.20 mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	6004 independent reflections
ω scans	4724 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$R_{int} = 0.066$
$T_{min} = 0.769$, $T_{max} = 0.850$	$\theta_{max} = 27.5°$
25 327 measured reflections	$h = -12 \rightarrow 12$
	$k = -29 \rightarrow 29$
	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 1.086P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.099$	$\Delta\rho_{max} = 0.34$ e Å^{-3}
$S = 1.04$	$\Delta\rho_{min} = -0.51$ e Å^{-3}
6004 reflections	
370 parameters	
H atoms treated by a mixture of independent and constrained refinement	

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···A	D—H	H···A	D···A	D—H···A
N9—H9···O40	0.88	2.00	2.848 (2)	160
N18—H18···O40^{i}	0.88	1.97	2.833 (2)	168
N27—H27···O31	0.88	2.03	2.848 (2)	155
O40—H40A···O32^{ii}	0.854 (19)	2.04 (2)	2.728 (2)	137.1 (16)
O40—H40B···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_{imine}—Fe—N_{imine} angles, and ω is the average of the three $N_{heterocycle}$—Fe—$N_{heterocycle}$ 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 $2\theta = 50°$. 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_{iso}(H) parameters were fixed at $1.2U_{eq}$(C,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···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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (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.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Deeney, F. A., Harding, C. J., Morgan, G. G., McKee, V., Nelson, J., Teat, S. J. & Clegg, W. (1998). *J. Chem. Soc. Dalton Trans.* pp. 1837–1844.
Elhaïk, J., Money, V. A., Barrett, S. A., Kilner, C. A., Radosavljevic Evans, I. & & Halcrow, M. A. (2003). *Dalton Trans.* pp. 2053–2060.
Holland, J. M., Barrett, S. A., Kilner, C. A. & Halcrow, M. A. (2002). *Inorg. Chem. Commun.* **5**, 328–332.
Holland, J. M., McAllister, J. A., Kilner, C. A., Thornton-Pett, M., Bridgeman, A. J. & Halcrow, M. A. (2002). *J. Chem. Soc. Dalton Trans.* pp. 548–554.
Holland, J. M., McAllister, J. A., Lu, Z., Kilner, C. A., Thornton-Pett, M. & Halcrow, M. A. (2001). *Chem. Commun.* pp. 577–578.
Ikuta, Y., Ooidemizu, M., Yamahata, Y., Yamada, M., Osa, S., Matsumoto, N., Iijima, S., Sunatsuki, Y., Kojima, M., Dahan, F. & Tuchagues, J.-P. (2003). *Inorg. Chem.* **42**, 7001–7017.
McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
Money, V. A., Elhaïk, J., Radosavljevic Evans, I., Halcrow, M. A. & Howard, J. A. K. (2004). *Dalton Trans.* pp. 65–69.
Money, V. A., Radosavljevic Evans, I., Halcrow, M. A., Goeta, A. E. & Howard, J. A. K. (2003). *Chem. Commun.* pp. 158–159.
Morgenstern-Badarau, I., Lambert, F., Deroche, A., Cesario, M., Guilhem, J., Keita, B. & Nadjo, L. (1998). *Inorg. Chim. Acta*, pp. 234–241, 275–276.
Morgenstern-Badarau, I., Lambert, F., Renault, J.-P., Cesario, M., Marechal, J.-D. & Maseras, F. (2000). *Inorg. Chim. Acta*, **297**, 338–350.
Nagasato, S., Katsuki, I., Motoda, Y., Sunatsuki, Y., Matsumoto, N. & Kojima, M. (2001). *Inorg. Chem.* **40**, 2534–2540.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Paul, S., Barik, A. K., Butcher, R. J. & Kar, S. K. (2000). *Polyhedron*, **19**, 2661–2666.
Paul, S., Barik, A. K., Peng, S. M. & Kar, S. K. (2002). *Inorg. Chem.* **41**, 5803–5809.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Smithson, R. J., Kilner, C. A., Brough, A. R. & Halcrow, M. A. (2003). *Polyhedron*, **22**, 725–733.
Sunatsuki, Y., Sakata, M., Matsuzaki, S., Matsumoto, N. & Kojima, M. (2001). *Chem. Lett.* pp. 1254–1255.
Yamada, M., Ooidemizu, M., Ikuta, Y., Osa, S., Matsumoto, N., Iijima, S., Kojima, M., Dahan, F. & Tuchagues, J.-P. (2003). *Inorg. Chem.* **42**, 8406–8416.
Yang, S.-P., Tong, Y.-X., Zhu, H.-L., Cao, H., Chen, X.-M. & Ji, L.-N. (2001). *Polyhedron*, **20**, 223–229.
Yukinari, S., Ikuta, Y., Matsumoto, N., Ohta, H., Kojima, M., Iijima, S., Hayami, S., Maeda, Y., Kaizaki, S., Dahan, F. & Tuchagues, J.-P. (2003). *Angew. Chem. Int. Ed.* **42**, 1614–1618.

supporting information

Acta Cryst. (2004). C**60**, m177–m179 [doi:10.1107/S010827010400407X]

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

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Computing details

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO*–SMN (Otwinowski & Minor, 1997); data reduction: *DENZO*–SMN; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

[Tris-(4-{pyrazol-3-yl}-3-aza-3-butenyl)amine]iron(II) diperchlorate hydrate

Crystal data

$C_{18}H_{24}FeN_{10}\cdot 2(ClO_4)\cdot H_2O$
$M_r = 653.24$
Monoclinic, $P2_1/n$
$a = 9.4086\ (1)$ Å
$b = 22.5317\ (4)$ Å
$c = 12.7279\ (2)$ Å
$\beta = 101.9858\ (6)°$
$V = 2639.38\ (7)$ Å^3
$Z = 4$
$F(000) = 1344$
$D_x = 1.644$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25327 reflections
$\theta = 1.8–27.5°$
$\mu = 0.84$ mm^{-1}
$T = 100$ K
Rectangular prism, yellow
0.33 × 0.23 × 0.20 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9.091 pixels mm^{-1}
Area detector scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.769$, $T_{max} = 0.850$
25327 measured reflections
6004 independent reflections
4724 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 27.5°$, $\theta_{min} = 1.8°$
$h = -12\rightarrow12$
$k = -29\rightarrow29$
$l = -16\rightarrow16$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.099$
$S = 1.04$
6004 reflections
370 parameters
4 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

$w = 1/[\sigma^2(F_o^2) + (0.047P)^2 + 1.086P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.51$ e Å^{-3}

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

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. No disorder was detected during refinement and no restraints were applied. All non-H atoms were refined anisotropically. All H atoms in the complex dication were placed in calculated positions and refined using a riding model. The two water H atoms [H40A and H40B] were located in the difference map and allowed to refine with the restraints O—H = 0.84 (1) Å and H···H = 1.37 (1) Å. An anti-bumping restraint was also applied between H9 and H40A.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Fe1	0.50212 (3)	0.366591 (12)	0.25044 (2)	0.01882 (9)
N2	0.42530 (18)	0.26732 (7)	0.12636 (12)	0.0219 (4)
C3	0.4007 (2)	0.21984 (9)	0.19870 (15)	0.0248 (4)
H3A	0.4267	0.1812	0.1708	0.030*
H3B	0.2965	0.2186	0.2019	0.030*
C4	0.4919 (2)	0.22993 (9)	0.31113 (15)	0.0240 (4)
H4A	0.4648	0.2009	0.3621	0.029*
H4B	0.5963	0.2249	0.3109	0.029*
N5	0.46352 (18)	0.29044 (7)	0.34325 (12)	0.0209 (4)
C6	0.4015 (2)	0.29873 (9)	0.42240 (15)	0.0219 (4)
H6	0.3760	0.2662	0.4622	0.026*
C7	0.3711 (2)	0.35947 (9)	0.44990 (15)	0.0207 (4)
N8	0.40373 (18)	0.40215 (7)	0.38485 (13)	0.0206 (4)
N9	0.36715 (18)	0.45327 (7)	0.42674 (13)	0.0222 (4)
H9	0.3779	0.4885	0.3997	0.027*
C10	0.3121 (2)	0.44404 (9)	0.51509 (16)	0.0238 (4)
H10	0.2786	0.4737	0.5571	0.029*
C11	0.3131 (2)	0.38397 (9)	0.53324 (15)	0.0228 (4)
H11	0.2816	0.3636	0.5896	0.027*
C12	0.5505 (2)	0.25584 (9)	0.07622 (16)	0.0262 (5)
H12A	0.5175	0.2345	0.0075	0.031*
H12B	0.6218	0.2304	0.1241	0.031*
C13	0.6227 (2)	0.31409 (9)	0.05553 (15)	0.0245 (4)
H13A	0.7098	0.3062	0.0255	0.029*
H13B	0.5543	0.3387	0.0037	0.029*
N14	0.66354 (18)	0.34474 (7)	0.15855 (13)	0.0216 (4)
C15	0.7954 (2)	0.35771 (9)	0.19791 (16)	0.0237 (4)
H15	0.8691	0.3523	0.1578	0.028*
C16	0.8291 (2)	0.38135 (9)	0.30735 (16)	0.0220 (4)
N17	0.71804 (18)	0.38498 (7)	0.35824 (13)	0.0216 (4)

N18	0.77857 (18)	0.40390 (7)	0.45793 (13)	0.0231 (4)
H18	0.7295	0.4103	0.5086	0.028*
C19	0.9228 (2)	0.41179 (9)	0.47085 (17)	0.0268 (5)
H19	0.9871	0.4246	0.5345	0.032*
C20	0.9602 (2)	0.39783 (10)	0.37475 (17)	0.0269 (5)
H20	1.0539	0.3991	0.3580	0.032*
C21	0.2919 (2)	0.28376 (9)	0.04891 (16)	0.0254 (5)
H21A	0.2325	0.2479	0.0269	0.030*
H21B	0.3176	0.3013	−0.0160	0.030*
C22	0.2045 (2)	0.32831 (9)	0.09948 (16)	0.0259 (5)
H22A	0.1180	0.3414	0.0462	0.031*
H22B	0.1714	0.3100	0.1610	0.031*
N23	0.29967 (18)	0.37886 (7)	0.13586 (13)	0.0219 (4)
C24	0.2685 (2)	0.43029 (9)	0.09623 (16)	0.0236 (4)
H24	0.1777	0.4382	0.0496	0.028*
C25	0.3778 (2)	0.47649 (9)	0.12542 (15)	0.0216 (4)
N26	0.50237 (18)	0.46036 (7)	0.19068 (13)	0.0218 (4)
N27	0.58740 (19)	0.50866 (7)	0.19898 (13)	0.0239 (4)
H27	0.6763	0.5103	0.2380	0.029*
C28	0.5205 (2)	0.55426 (9)	0.14045 (17)	0.0274 (5)
H28	0.5604	0.5925	0.1339	0.033*
C29	0.3841 (2)	0.53545 (9)	0.09208 (17)	0.0282 (5)
H29	0.3102	0.5575	0.0462	0.034*
Cl30	0.96490 (6)	0.53235 (2)	0.20209 (4)	0.02860 (13)
O31	0.87955 (18)	0.54411 (8)	0.28247 (13)	0.0412 (4)
O32	1.10489 (18)	0.51063 (8)	0.25561 (15)	0.0435 (4)
O33	0.89253 (18)	0.48819 (7)	0.12910 (12)	0.0345 (4)
O34	0.9830 (2)	0.58560 (8)	0.14540 (15)	0.0525 (5)
Cl35	0.50340 (5)	0.71869 (2)	0.23985 (4)	0.02391 (12)
O36	0.40823 (18)	0.66807 (7)	0.23031 (15)	0.0403 (4)
O37	0.62998 (17)	0.70271 (8)	0.19977 (13)	0.0378 (4)
O38	0.5450 (2)	0.73624 (8)	0.35028 (12)	0.0420 (4)
O39	0.42776 (18)	0.76658 (7)	0.17823 (12)	0.0338 (4)
O40	0.34003 (17)	0.57388 (7)	0.35871 (12)	0.0265 (3)
H40A	0.260 (2)	0.5725 (9)	0.3126 (18)	0.048 (8)*
H40B	0.391 (3)	0.5997 (13)	0.336 (2)	0.075 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Fe1	0.01900 (17)	0.02036 (16)	0.01707 (15)	−0.00015 (11)	0.00369 (11)	0.00102 (11)
N2	0.0245 (9)	0.0242 (9)	0.0168 (8)	−0.0015 (7)	0.0040 (7)	0.0002 (7)
C3	0.0328 (12)	0.0208 (10)	0.0212 (10)	−0.0048 (9)	0.0063 (9)	−0.0016 (8)
C4	0.0330 (12)	0.0191 (10)	0.0200 (10)	0.0027 (9)	0.0056 (9)	−0.0001 (8)
N5	0.0235 (9)	0.0215 (8)	0.0169 (8)	0.0011 (7)	0.0022 (7)	−0.0005 (6)
C6	0.0250 (10)	0.0225 (10)	0.0172 (9)	−0.0027 (8)	0.0022 (8)	0.0029 (8)
C7	0.0182 (10)	0.0247 (10)	0.0185 (9)	−0.0002 (8)	0.0023 (8)	0.0017 (8)
N8	0.0212 (9)	0.0209 (8)	0.0196 (8)	0.0008 (7)	0.0038 (7)	−0.0008 (7)

N9	0.0237 (9)	0.0200 (8)	0.0225 (8)	0.0006 (7)	0.0042 (7)	−0.0014 (7)
C10	0.0234 (11)	0.0267 (11)	0.0222 (10)	0.0017 (9)	0.0065 (8)	−0.0025 (8)
C11	0.0222 (10)	0.0277 (11)	0.0187 (9)	0.0010 (9)	0.0047 (8)	−0.0002 (8)
C12	0.0336 (12)	0.0248 (11)	0.0211 (10)	−0.0022 (9)	0.0076 (9)	−0.0040 (8)
C13	0.0260 (11)	0.0292 (11)	0.0185 (9)	−0.0007 (9)	0.0052 (8)	−0.0041 (8)
N14	0.0245 (9)	0.0222 (9)	0.0181 (8)	0.0001 (7)	0.0043 (7)	−0.0003 (6)
C15	0.0235 (11)	0.0248 (10)	0.0243 (10)	0.0010 (9)	0.0081 (9)	0.0004 (8)
C16	0.0218 (10)	0.0218 (10)	0.0219 (10)	0.0013 (8)	0.0031 (8)	0.0000 (8)
N17	0.0232 (9)	0.0225 (9)	0.0181 (8)	−0.0001 (7)	0.0022 (7)	−0.0022 (7)
N18	0.0260 (9)	0.0248 (9)	0.0179 (8)	0.0024 (7)	0.0029 (7)	−0.0030 (7)
C19	0.0250 (11)	0.0280 (11)	0.0246 (10)	−0.0022 (9)	−0.0010 (8)	−0.0028 (8)
C20	0.0205 (10)	0.0307 (11)	0.0288 (11)	0.0003 (9)	0.0035 (9)	−0.0021 (9)
C21	0.0265 (11)	0.0275 (11)	0.0202 (10)	−0.0064 (9)	0.0002 (8)	−0.0012 (8)
C22	0.0234 (11)	0.0289 (11)	0.0235 (10)	−0.0041 (9)	0.0005 (8)	0.0026 (8)
N23	0.0215 (9)	0.0249 (9)	0.0190 (8)	−0.0036 (7)	0.0037 (7)	−0.0010 (7)
C24	0.0217 (10)	0.0282 (11)	0.0202 (10)	0.0028 (9)	0.0028 (8)	0.0031 (8)
C25	0.0229 (10)	0.0233 (10)	0.0193 (9)	0.0004 (8)	0.0058 (8)	0.0002 (8)
N26	0.0228 (9)	0.0228 (9)	0.0200 (8)	−0.0029 (7)	0.0051 (7)	−0.0005 (7)
N27	0.0234 (9)	0.0255 (9)	0.0229 (9)	−0.0044 (7)	0.0052 (7)	−0.0018 (7)
C28	0.0328 (12)	0.0211 (10)	0.0295 (11)	−0.0004 (9)	0.0093 (9)	0.0013 (8)
C29	0.0300 (12)	0.0241 (11)	0.0296 (11)	0.0024 (9)	0.0046 (9)	0.0024 (9)
Cl30	0.0260 (3)	0.0301 (3)	0.0283 (3)	−0.0040 (2)	0.0023 (2)	−0.0015 (2)
O31	0.0294 (9)	0.0597 (12)	0.0342 (9)	−0.0028 (8)	0.0063 (7)	−0.0178 (8)
O32	0.0253 (9)	0.0500 (11)	0.0510 (11)	−0.0012 (8)	−0.0018 (8)	0.0030 (9)
O33	0.0373 (9)	0.0349 (9)	0.0300 (8)	−0.0085 (7)	0.0042 (7)	−0.0078 (7)
O34	0.0712 (14)	0.0317 (10)	0.0505 (11)	−0.0119 (9)	0.0036 (10)	0.0095 (8)
Cl35	0.0304 (3)	0.0218 (2)	0.0210 (2)	0.0003 (2)	0.0089 (2)	−0.00018 (18)
O36	0.0387 (10)	0.0283 (9)	0.0586 (11)	−0.0065 (7)	0.0206 (8)	0.0012 (8)
O37	0.0300 (9)	0.0482 (10)	0.0395 (9)	−0.0008 (8)	0.0168 (7)	−0.0046 (8)
O38	0.0658 (12)	0.0397 (10)	0.0182 (8)	0.0187 (9)	0.0033 (8)	−0.0022 (7)
O39	0.0468 (10)	0.0296 (8)	0.0234 (8)	0.0057 (7)	0.0041 (7)	0.0062 (6)
O40	0.0264 (8)	0.0281 (8)	0.0252 (8)	−0.0032 (7)	0.0054 (7)	0.0011 (6)

Geometric parameters (Å, º)

Fe1—N2	2.7468 (17)	C16—N17	1.341 (3)
Fe1—N5	2.1563 (16)	C16—C20	1.398 (3)
Fe1—N8	2.2547 (16)	N17—N18	1.348 (2)
Fe1—N14	2.1575 (17)	N18—C19	1.344 (3)
Fe1—N17	2.2413 (17)	N18—H18	0.8800
Fe1—N23	2.1628 (17)	C19—C20	1.377 (3)
Fe1—N26	2.2457 (16)	C19—H19	0.9500
N2—C3	1.461 (2)	C20—H20	0.9500
N2—C21	1.473 (3)	C21—C22	1.522 (3)
N2—C12	1.475 (3)	C21—H21A	0.9900
C3—C4	1.525 (3)	C21—H21B	0.9900
C3—H3A	0.9900	C22—N23	1.463 (3)
C3—H3B	0.9900	C22—H22A	0.9900

C4—N5	1.464 (2)	C22—H22B	0.9900
C4—H4A	0.9900	N23—C24	1.273 (3)
C4—H4B	0.9900	C24—C25	1.456 (3)
N5—C6	1.278 (3)	C24—H24	0.9500
C6—C7	1.456 (3)	C25—N26	1.339 (3)
C6—H6	0.9500	C25—C29	1.400 (3)
C7—N8	1.345 (2)	N26—N27	1.342 (2)
C7—C11	1.403 (3)	N27—C28	1.346 (3)
N8—N9	1.344 (2)	N27—H27	0.8800
N9—C10	1.349 (3)	C28—C29	1.370 (3)
N9—H9	0.8800	C28—H28	0.9500
C10—C11	1.373 (3)	C29—H29	0.9500
C10—H10	0.9500	Cl30—O34	1.4282 (17)
C11—H11	0.9500	Cl30—O33	1.4332 (15)
C12—C13	1.526 (3)	Cl30—O32	1.4372 (17)
C12—H12A	0.9900	Cl30—O31	1.4502 (17)
C12—H12B	0.9900	Cl35—O39	1.4332 (15)
C13—N14	1.461 (2)	Cl35—O38	1.4341 (16)
C13—H13A	0.9900	Cl35—O37	1.4355 (16)
C13—H13B	0.9900	Cl35—O36	1.4394 (16)
N14—C15	1.272 (3)	O40—H40A	0.854 (19)
C15—C16	1.463 (3)	O40—H40B	0.84 (2)
C15—H15	0.9500		

N2—Fe1—N5	67.23 (5)	C12—C13—H13B	110.3
N2—Fe1—N8	128.69 (5)	H13A—C13—H13B	108.5
N2—Fe1—N14	68.49 (6)	C15—N14—C13	121.04 (18)
N2—Fe1—N17	126.82 (6)	C15—N14—Fe1	118.23 (14)
N2—Fe1—N23	68.08 (6)	C13—N14—Fe1	120.70 (13)
N2—Fe1—N26	126.16 (5)	N14—C15—C16	117.34 (19)
N5—Fe1—N8	74.02 (6)	N14—C15—H15	121.3
N5—Fe1—N14	109.45 (6)	C16—C15—H15	121.3
N5—Fe1—N17	92.64 (6)	N17—C16—C20	111.33 (18)
N5—Fe1—N23	104.25 (6)	N17—C16—C15	116.45 (18)
N5—Fe1—N26	161.14 (6)	C20—C16—C15	132.05 (19)
N8—Fe1—N14	159.82 (6)	C16—N17—N18	104.75 (16)
N8—Fe1—N17	86.13 (6)	C16—N17—Fe1	113.02 (12)
N8—Fe1—N23	91.34 (6)	N18—N17—Fe1	141.91 (13)
N8—Fe1—N26	87.25 (6)	C19—N18—N17	112.05 (17)
N14—Fe1—N17	73.95 (6)	C19—N18—H18	124.0
N14—Fe1—N23	106.51 (6)	N17—N18—H18	124.0
N14—Fe1—N26	88.90 (6)	N18—C19—C20	107.36 (18)
N17—Fe1—N23	161.53 (7)	N18—C19—H19	126.3
N17—Fe1—N26	88.21 (6)	C20—C19—H19	126.3
N23—Fe1—N26	73.39 (6)	C19—C20—C16	104.49 (19)
C3—N2—C21	112.40 (16)	C19—C20—H20	127.8
C3—N2—C12	112.93 (16)	C16—C20—H20	127.8
C21—N2—C12	113.64 (15)	N2—C21—C22	110.05 (16)

C3—N2—Fe1	106.93 (11)	N2—C21—H21A	109.7
C21—N2—Fe1	105.42 (12)	C22—C21—H21A	109.7
C12—N2—Fe1	104.67 (11)	N2—C21—H21B	109.7
N2—C3—C4	110.50 (16)	C22—C21—H21B	109.7
N2—C3—H3A	109.5	H21A—C21—H21B	108.2
C4—C3—H3A	109.5	N23—C22—C21	107.35 (16)
N2—C3—H3B	109.5	N23—C22—H22A	110.2
C4—C3—H3B	109.5	C21—C22—H22A	110.2
H3A—C3—H3B	108.1	N23—C22—H22B	110.2
N5—C4—C3	107.54 (16)	C21—C22—H22B	110.2
N5—C4—H4A	110.2	H22A—C22—H22B	108.5
C3—C4—H4A	110.2	C24—N23—C22	120.48 (17)
N5—C4—H4B	110.2	C24—N23—Fe1	118.79 (14)
C3—C4—H4B	110.2	C22—N23—Fe1	120.62 (13)
H4A—C4—H4B	108.5	N23—C24—C25	117.20 (18)
C6—N5—C4	119.71 (17)	N23—C24—H24	121.4
C6—N5—Fe1	118.15 (13)	C25—C24—H24	121.4
C4—N5—Fe1	121.81 (12)	N26—C25—C29	111.04 (18)
N5—C6—C7	118.14 (18)	N26—C25—C24	116.44 (17)
N5—C6—H6	120.9	C29—C25—C24	132.33 (19)
C7—C6—H6	120.9	C25—N26—N27	105.05 (16)
N8—C7—C11	111.00 (18)	C25—N26—Fe1	113.78 (13)
N8—C7—C6	116.28 (17)	N27—N26—Fe1	141.17 (13)
C11—C7—C6	132.72 (19)	N26—N27—C28	111.88 (17)
N9—N8—C7	104.99 (15)	N26—N27—H27	124.1
N9—N8—Fe1	141.73 (13)	C28—N27—H27	124.1
C7—N8—Fe1	113.26 (13)	N27—C28—C29	107.42 (19)
N8—N9—C10	111.92 (16)	N27—C28—H28	126.3
N8—N9—H9	124.0	C29—C28—H28	126.3
C10—N9—H9	124.0	C28—C29—C25	104.61 (19)
N9—C10—C11	107.56 (18)	C28—C29—H29	127.7
N9—C10—H10	126.2	C25—C29—H29	127.7
C11—C10—H10	126.2	O34—Cl30—O33	110.25 (11)
C10—C11—C7	104.53 (18)	O34—Cl30—O32	109.39 (12)
C10—C11—H11	127.7	O33—Cl30—O32	109.64 (10)
C7—C11—H11	127.7	O34—Cl30—O31	110.14 (12)
N2—C12—C13	110.35 (17)	O33—Cl30—O31	109.02 (10)
N2—C12—H12A	109.6	O32—Cl30—O31	108.36 (11)
C13—C12—H12A	109.6	O39—Cl35—O38	109.39 (9)
N2—C12—H12B	109.6	O39—Cl35—O37	110.41 (10)
C13—C12—H12B	109.6	O38—Cl35—O37	109.87 (11)
H12A—C12—H12B	108.1	O39—Cl35—O36	108.72 (10)
N14—C13—C12	107.18 (16)	O38—Cl35—O36	109.84 (11)
N14—C13—H13A	110.3	O37—Cl35—O36	108.59 (10)
C12—C13—H13A	110.3	H40A—O40—H40B	106.0 (15)
N14—C13—H13B	110.3		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N9—H9···O40	0.88	2.00	2.848 (2)	160
N18—H18···O40^{i}	0.88	1.97	2.833 (2)	168
N27—H27···O31	0.88	2.03	2.848 (2)	155
O40—H40*A*···O32^{ii}	0.85 (2)	2.04 (2)	2.728 (2)	137 (2)
O40—H40*B*···O36	0.84 (2)	2.07 (2)	2.832 (2)	149 (2)

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) *x*−1, *y*, *z*.