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Key indicators

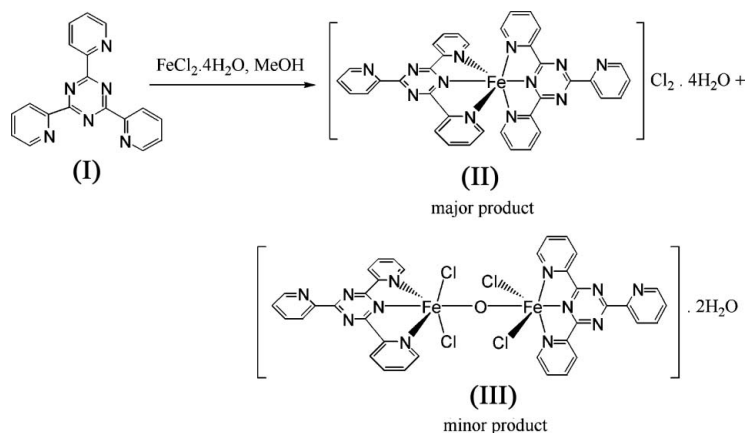
Single-crystal X-ray study
 $T = 84\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
Disorder in solvent or counterion
 R factor = 0.042
 wR factor = 0.125
Data-to-parameter ratio = 15.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. μ -Oxo-bis[*trans*-dichloro(2,4,6-tri-2-pyridyl-
1,3,5-triazine)iron(III)] dihydrate

Two iron complexes of the tridentate ligand 2,4,6-tri-2-pyridyl-1,3,5-triazine (tpt, $\text{C}_{18}\text{H}_{12}\text{N}_6$) have been isolated and characterized. One is $[\text{Fe}^{\text{II}}(\text{tpt})_2]\text{Cl}_2 \cdot 4\text{H}_2\text{O}$, (II), and the other is the title dinuclear complex, $[\text{Fe}^{\text{III}}_2\text{Cl}_4(\mu\text{-O})(\text{tpt})] \cdot 2\text{H}_2\text{O}$, (III), which has been crystallographically characterized. The coordination sphere around each Fe atom is a distorted octahedron formed by three N atoms from the tridentate site of one tpt ligand, coordinated in a meridional fashion, two Cl^- ions *cis* to the central donor of the tpt ligand, and an oxo bridging ligand *trans* to the tpt ligand. The Fe–N distances are in the range 2.124 (2)–2.202 (3) Å, the Fe–O–Fe angle is 176.13 (14)° and the Fe···Fe separation is 3.536 (2) Å.

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Comment

Dark-blue prisms of the iron complex, (II), and occasionally red rod-like crystals of the title compound, (III), were obtained from the reaction of (I) with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in MeOH (see scheme).



The proposed structure of the new iron complex, (II), is that of a complex with Fe bound in the terpyridyl sites of two tpt ligands, leaving the bidentate site of the ligand uncoordinated. ^1H NMR and ^{13}C NMR spectroscopy, electrospray ionization mass spectra and elemental analysis of the complex are all consistent with this structure. X-ray crystallographic studies of the dark-blue crystals support this assignment, but the marginal quality of the crystals meant that, while a structural solution could be found, the refinement was unsatisfactory ($R \approx 0.15$).

A crystallographic study of the red minor product met with more success. The complex $[\{\text{Fe}(\text{tpt})\text{Cl}_2\}_2(\mu\text{-O})] \cdot 2\text{H}_2\text{O}$, (III), is shown in Fig. 1. Each Fe^{III} ion is meridionally coordinated to the tridentate terpyridyl site of the ligand tpt, (I), in the

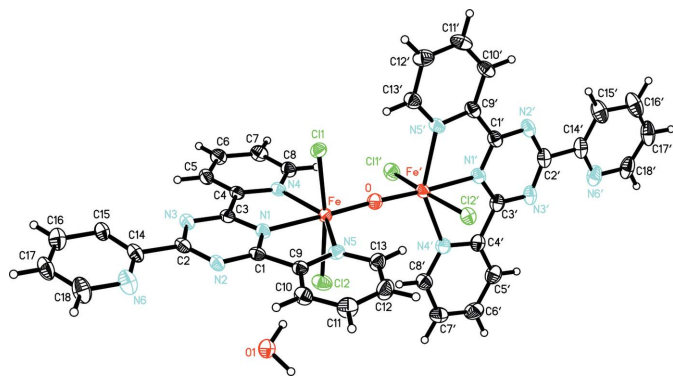


Figure 1

A perspective view of the diiron oxo-bridged complex, (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. One disordered solvent water molecule in the asymmetric unit has been omitted for clarity.

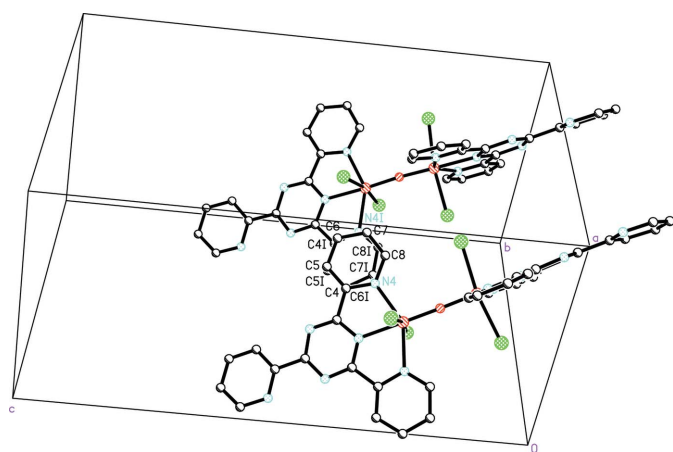


Figure 2

The π - π stacking interactions between the flanking pyridyl rings of adjacent neutral molecules in a cell. The plane-to-plane separation distance between flanking pyridyl rings is 3.550 (5) Å [face-to-face and centroid-to-centroid = 3.890 (5) Å]. H atoms have been omitted. [Symmetry code: (I) $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$.]

complex. The fourth and the fifth coordination sites of each Fe^{III} ion are occupied by two Cl⁻ ions, *cis* to the central donor of the tpt ligand. The bridging oxide ligand is coordinated *trans* to the central donor of the tpt ligand. Bond angles show that the coordination at each Fe centre deviates from that of an ideal octahedron (Table 1); the Fe \cdots Fe separation is 3.536 (2) Å.

There are two water molecules in the asymmetric unit, one of which is highly disordered. There is an extensive hydrogen-bonding network involving the ordered water molecules and coordinated Cl⁻ ions (Table 2).

The Fe—O—Fe angle [176.13 (14)°] and Fe—O bond lengths [1.767 (2) and 1.769 (2) Å] are in the ranges observed for similar oxo-bridged polypyridyl complexes of Fe^{III} (Table 3). On the other hand, the Fe—Cl bond distances in the structure of (III) [2.399 (1) and 2.419 (1) Å on one side of the complex, and 2.405 (1) and 2.416 (1) Å on the other] are significantly longer than literature values (Table 3).

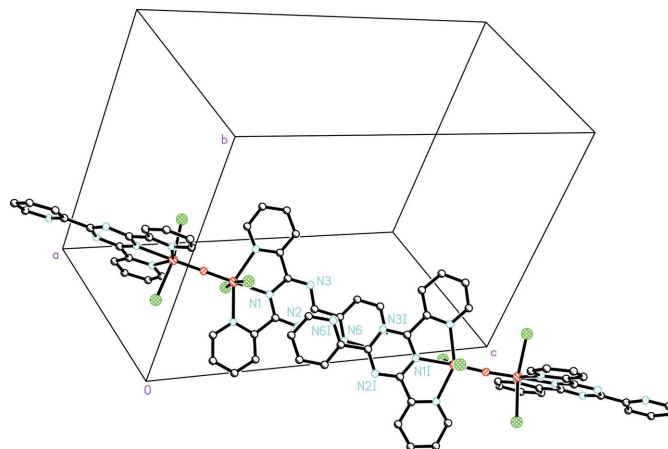


Figure 3

The π - π stacking interactions between the central triazine ring of one molecule in one cell and the terminal pyridyl ring of an adjacent molecule in an adjacent cell. The plane-to-plane separation is 3.451 (5) Å [face-to-face and centroid-to-centroid = 4.013 (5) Å]. H atoms have been omitted. [Symmetry code: (I) $1 + x, \frac{1}{2} - y, -\frac{1}{2} + z$.]

In the structure of (III), the shortest Fe—N bond lengths are those to the central triazine ring in the tpt ligands. This observation is consistent with other metal-tpt complexes (Chirayil *et al.*, 1991; Hartshorn *et al.*, 2005; Paul *et al.*, 1997; Polson *et al.*, 2004; Hartshorn & Zibaseresht, 2006; Zibaseresht & Hartshorn, 2005*a,b*).

There are two kinds of π - π stacking interactions (face-to-face) between adjacent neutral molecules. Firstly, there are π - π stacking interactions between the flanking pyridyl rings of adjacent neutral molecules in the same unit cell, with a plane-to-plane separation of 3.550 (5) Å [centroid-to-centroid 3.890 (5) Å] (Fig. 2). Secondly, there are π - π stacking interactions between the central triazine and terminal pyridyl rings of one molecule in one cell and the terminal pyridyl and central triazine rings of the symmetry-related molecule at $(1 + x, \frac{1}{2} - y, -\frac{1}{2} + z)$ in an adjacent cell. The plane-to-plane separations are both 3.451 (5) Å [centroid-to-centroid 4.013 (5) Å], as they are related by symmetry (Fig. 3).

Experimental

FeCl₂·4H₂O (0.199 g, 1 mmol) in MeOH (5 ml) was added dropwise with stirring to a solution of tpt, (I) (Case & Koft, 1959; Polson *et al.*, 2002) (0.624 g, 2 mmol), in MeOH (10 ml). The resulting deep-purple solution was stirred for 4 h at room temperature. The reaction mixture was evaporated to dryness at reduced pressure and then redissolved in water. Dark-blue prisms of (II) and then some red block-like crystals of (III) were obtained by slow evaporation of the solution. Crystals of (II) were collected by filtration, washed with diethyl ether and air-dried. ¹H NMR [300 MHz, D₂O, 3-(trimethylsilyl)-1-propane sulfonic acid (TPMS) (internal reference), δ , p.p.m.]: 9.40 (2H, *d*), 9.23 (4H, *d*), 9.09 (2H, *d*), 8.43 (2H, *dd*), 8.15 (4H, *dd*), 7.99 (2H, *dd*), 7.57 (4H, *dd*), 7.37 (4H, *dd*); ¹³C NMR (75 MHz, D₂O, δ , p.p.m.): 178.48, 173.19, 157.55, 156.46, 153.42, 153.16, 142.67, 142.24, 133.07, 131.73, 131.09, 129.44. ESI-MS, *m/z* [intensity (%), fragment] 715.0875 [3, (*M* - 2Cl)⁺], 340.0758 [100, (*M* - 2Cl)²⁺]. Elemental analysis, found: C 52.12, H 4.03, N 20.20%; calculated for C₃₆H₃₂Cl₂FeN₁₂O₄: C 52.51, H 3.92, N 20.41%. A small quantity of

red rod-like crystals of (III) suitable for X-ray analysis were also obtained from the same reaction mixture. Further characterization of this complex was not pursued due to poor solubility in common solvents.

Crystal data

[Fe₂Cl₄O(C₁₈H₁₂N₆)₂].2H₂O
M_r = 928.19
 Monoclinic, *P*2₁/*c*
a = 10.8726 (11) Å
b = 15.8656 (16) Å
c = 22.747 (2) Å
 β = 93.135 (2)°
V = 3918.0 (7) Å³

Z = 4
D_x = 1.574 Mg m⁻³
 Mo *K*α radiation
 μ = 1.07 mm⁻¹
T = 84 (2) K
 Block, red
 0.45 × 0.35 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
T_{min} = 0.699, *T_{max}* = 0.90

34106 measured reflections
 7995 independent reflections
 6159 reflections with *I* > 2σ(*I*)
R_{int} = 0.041
 θ_{max} = 26.4°

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.042
wR(*F*²) = 0.125
S = 1.05
 7995 reflections
 531 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2 + 4.758P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 1.47 \text{ e \AA}^{-3}$
 $\Delta\rho_{min} = -0.44 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Fe—O	1.767 (2)	Fe'—O	1.769 (2)
Fe—N1	2.124 (2)	Fe'—N1'	2.127 (3)
Fe—N5	2.186 (3)	Fe'—N4'	2.188 (3)
Fe—N4	2.202 (3)	Fe'—N5'	2.193 (3)
Fe—Cl2	2.3999 (9)	Fe'—Cl1'	2.4051 (10)
Fe—Cl1	2.4187 (9)	Fe'—Cl2'	2.4162 (10)
O—Fe—N1	178.68 (10)	O—Fe'—N4'	109.86 (10)
O—Fe—N5	108.07 (10)	N1'—Fe'—N4'	73.06 (10)
N1—Fe—N5	72.91 (10)	O—Fe'—N5'	104.16 (10)
O—Fe—N4	105.97 (10)	N1'—Fe'—N5'	72.92 (10)
N1—Fe—N4	73.04 (9)	N4'—Fe'—N5'	145.95 (10)
N5—Fe—N4	145.94 (10)	O—Fe'—Cl1'	95.01 (8)
O—Fe—Cl2	94.97 (8)	N1'—Fe'—Cl1'	84.88 (8)
N1—Fe—Cl2	85.95 (7)	N4'—Fe'—Cl1'	86.72 (8)
N5—Fe—Cl2	86.50 (7)	N5'—Fe'—Cl1'	91.64 (8)
N4—Fe—Cl2	91.70 (7)	O—Fe'—Cl2'	95.02 (8)
O—Fe—Cl1	95.13 (8)	N1'—Fe'—Cl2'	85.36 (8)
N1—Fe—Cl1	84.01 (7)	N4'—Fe'—Cl2'	85.08 (8)
N5—Fe—Cl1	86.77 (7)	N5'—Fe'—Cl2'	90.86 (8)
N4—Fe—Cl1	89.17 (7)	Cl1'—Fe'—Cl2'	168.74 (4)
Cl2—Fe—Cl1	169.21 (3)	Fe—O—Fe'	176.13 (14)
O—Fe'—N1'	177.07 (11)		

Table 2

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>
O1—H1B...Cl2	0.87 (2)	2.28 (2)	3.151 (3)	176 (4)
O1—H1A...Cl1 ⁱ	0.88 (2)	2.32 (2)	3.200 (3)	177 (4)

Symmetry code: (i) $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$.

Table 3

Comparison of geometric parameters from the literature (Å, °).

Compound†	Fe—O—Fe	Fe—O	Fe—Cl
<i>A</i>	180.0	1.805 (1)	2.293 (1)
<i>B</i>	180.0	1.779 (1)	2.348 (3)
<i>C</i>	167.4 (4)	1.786 (2)	2.328 (3)
<i>D</i>	176.43 (8)	1.811 (1) and 1.814 (1)	2.324 (1) and 2.334 (1)
<i>E</i>	174.7 (5)	1.785 (1)	2.298 (2)
<i>F</i>	161 (1)	1.787 (6)	2.34 (1)
<i>G</i>	178.6 (4)	1.782 (1)	2.284 (1)
<i>H</i>	176.0 (5)	1.800 (8) and 1.794 (8)	2.289 (4) and 2.304 (4)
<i>I</i>	180.0	1.780 (2)	2.276 (2)
<i>J</i>	180.0	1.790 (1)	2.319 (4)
<i>K</i>	180.0	1.80 (1)	2.31 (1)
<i>L</i>	180.0	1.788 (4)	2.299 (1)
<i>M</i>	177.76	1.603	2.352
<i>N</i>	180.0	1.782 (1)	2.285 (1)
<i>O</i>	166.91	1.788 (4) and 1.784 (4)	2.325 (2) and 2.315 (2)

† *A* = (μ₂-oxo)dichlorobis[tris(benzimidazol-2-yl)methyl]amine]diiron(III) bis(hexafluorophosphate) tetrahydrofuran solvate (Buchanan *et al.*, 1993); *B* = (μ₂-oxo)-bis[(2,2':6',2'':6'',2''':6'''-quaterpyridine)chloroiron] diperchlorate dihydrate (Che *et al.*, 1995); *C* = (μ₂-oxo)bis[chlorobis(4,4'-dimethyl-2,2'-bipyridine)iron(III)] bis(hexafluorophosphate) (Collomb *et al.*, 1999); *D* = (μ₂-oxo)bis[chloro(*N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine)iron(III)] diperchlorate hydrate (Egdal *et al.*, 2002); *E* = (μ₂-oxo)dichlorobis[tris(2-pyridylmethyl)amine-*N,N',N'',N'''*]diiron(III)] diperchlorate (Hazell *et al.*, 1994); *F* = (μ₂-oxo)bis[*cis*-chlorobis(1,10-phenanthroline-*N,N'*)iron(III)] dichloride hydrate (Healy *et al.*, 1983); *G* = (μ₂-oxo)dichlorobis[bis[2-(2-pyridyl)methyl]amine]diiron(III)] dichloride methanol solvate (Hemmert *et al.*, 1999); *H* = (μ₂-oxo)bis[*N*-[2-[bis(2-pyridylmethyl)amino]ethyl]morpholine]chloroiron(III)] diperchlorate (Ito *et al.*, 1996); *I* = (μ₂-oxo)bis[[*N,N'*-bis(2-pyridylmethyl)glycinamide]chloroiron(III)] diperchlorate dihydrate (Ito *et al.*, 1996); *J* = bis[dichloro[tris(2-pyridylmethyl)amine]iron](μ₂-oxo)bis[chloro[tris(2-pyridylmethyl)amine]iron] tetraepchlorate (Kojima *et al.*, 1993); *K* = (μ₂-oxo)dichlorobis[[tris(2-benzimidazolylmethyl)amine]iron] diperchlorate methanol solvate dihydrate (Kwak *et al.*, 1999); *L* = (μ₂-oxo)bis[chlorobis(2-pyridylmethyl)[(1-methylimidazol-2-yl)methylamine-*N,N',N''*]-*N'''*]iron(III)] dichloride methanol solvate (Pascaly *et al.*, 1999); *M* = (μ₂-oxo)-dichlorobis[*N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine]diiron(III) dichloride acetonitrile solvate pentahydrate (Raffard *et al.*, 2002); *N* = (μ₂-oxo)bis[2-[bis(benzimidazol-2-ylmethyl)amino]ethanol-*N,N',N''*,*O*]chloroiron(III)] dinitrate (Takahashi *et al.*, 1985); *O* = (μ₂-oxo)bis[bis(2,2'-bipyridyl)chloroiron(III)] diperchlorate acetonitrile methanol solvate hydrate (Xiang *et al.*, 1998).

The disordered water molecule was refined with site occupancies of 0.7 (1) and 0.3 (1). However, the anisotropic displacement parameters of the disordered O atoms were large. Several attempts at defining additional sites or using lower site-occupancy factors for the disordered O atoms yielded inferior results. All H atoms bonded to C atoms were placed in calculated positions, with C—H = 0.93 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C), and were included in the refinement in the riding-model approximation. The H atoms of the disordered water molecule could not be located in the difference Fourier map. The ordered water H atoms were, however, found in the difference map and their positions were refined with a restrained geometry, with O—H = 0.85 (1) Å and *U*_{iso}(H) = 1.2*U*_{eq}(O). The highest peak is located 1.34 Å from atom O2.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXTL (Sheldrick, 2001); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

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