Hexakis(1-methylimidazole-κN^3)iron(II) dichloride dihydrate

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The title compound, [Fe($C_4H_6N_2$)$_6$]Cl$_2$·2H$_2$O, contains discrete ions and molecules and is isostructural with its Co, Ni and Ru analogues. The Fe^{II} atom (site symmetry $\bar{1}$) is octahedrally coordinated by six 1-methylimidazole ligands. An anionic O—H···Cl hydrogen-bonded assembly formed by two chloride ions and two water molecules completes the structure.

Comment

Complexes of divalent metal ions such as copper, nickel, cobalt, zinc or iron with imidazole and its derivatives have attracted attention because of their relation to a variety of biologically important molecules which involve the bonding of the metal ion with the imidazole rings of the histidine unit (Sundberg & Martin, 1974). Ruthenium complexes with imidazole ligands are of interest for their biochemical activity (Clarke *et al.*, 1996). A protein purification method, known as immobilized-metal-ion affinity chromatography (IMAC) and based on the binding of, *e.g.*, histidine to immobilized metal ions, provides another source of interest. The use of imidazole and its derivatives (good ligands for a range of metals) may also be considered as a convenient approach for the construction of supramolecular architectures.

(I)
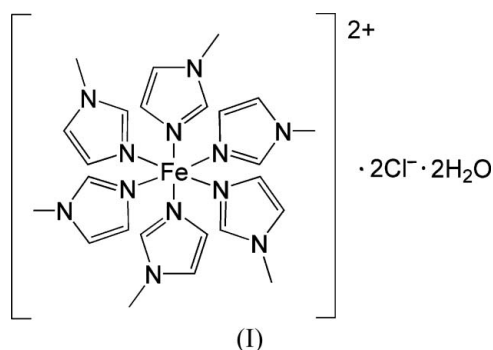
For the chlorides of complex cations, in which the divalent metal is octahedrally coordinated by six imidazole (Imid) or six 1-methylimidazole (1-MeImid) ligands, the selective formation of either tetrahydrates (Imid) or dihydrates (1-MeImid) has been observed. Tetrahydrates with the overall formula [M(Imid)$_6$]Cl$_2$·4H$_2$O have been described for M = Fe^{II} (Jian *et al.*, 2004) and Co^{II} (Zhu *et al.*, 2003), Ni^{II} (Gong *et al.*, 2005) as well as for Mn^{II} and Zn^{II} (Garrett *et al.*, 1983). All adopt the same triclinic structure type in which layers of complex cations alternate with layers of hydrogen-bonded chloride ions and water molecules. The layers are connected by N—H···Cl hydrogen bonds.
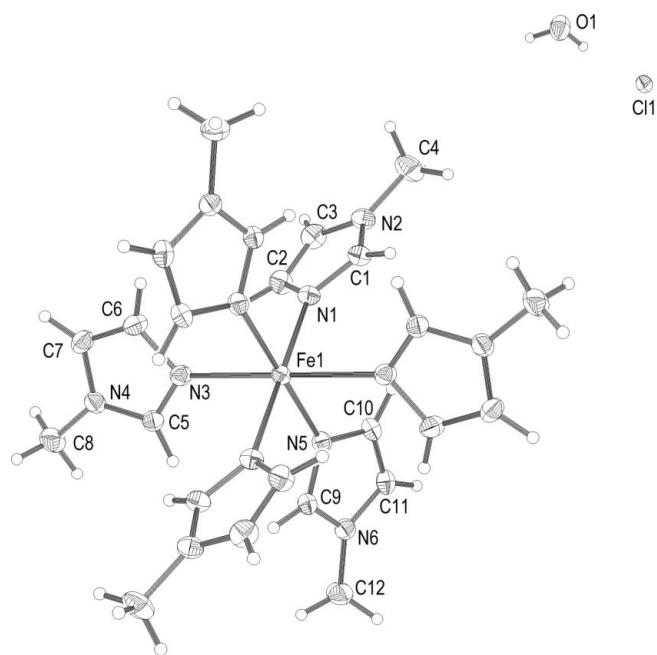
Figure 1
The structure of the components of (I), showing 50% displacement ellipsoids (arbitrary spheres for the H atoms). Unlabelled atoms are generated by the symmetry code $(-x, -y, -z)$.
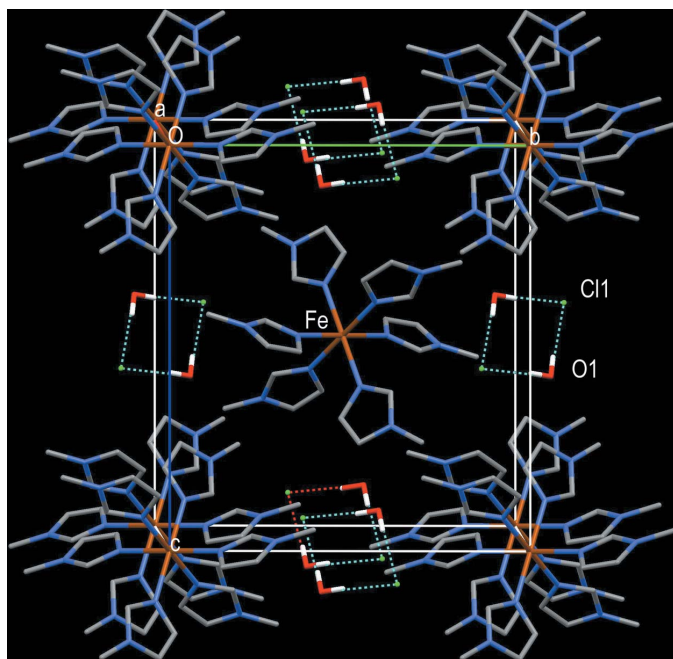

Figure 2
A packing diagram of (I) viewed along the a axis. H atoms (except water) have been omitted. Dashed lines indicate hydrogen bonds. Colour code: C grey, N blue, Fe brown, Cl green, O red and H white.

Three isomorphous dihydrates of overall formula $[M(1\text{-}MeImid)_6]Cl_2 \cdot 2H_2O$ have been reported where $M = Co^{II}$ (Marzotto *et al.*, 1989), Ru^{II} (Clarke *et al.*, 1996) and, very recently, Ni^{II} (Wang *et al.*, 2006). The title compound, (I) (Fig. 1), with $M = Fe^{II}$ complements this isostructural family. It

follows that, as observed for the other three dihydrates, the monoclinic crystal structure of (I) is composed of discrete $[Fe(1\text{-}MeImid)_6]^{2+}$ complex cations accompanied by charge-balancing chloride ions and water molecules.

Since the Fe atom occupies an inversion centre, three independent 1-methylimidazole ligands generate a distorted octahedral environment with N—Fe—N angles close to 90° and opposite imidazole rings lying in the same plane. The M—N bonds in (I) (Table 1) are the longest found in these four isomorphous compounds, which follow the order Fe > Co > Ni > Ru.

The structure of (I) is completed by an anionic assembly formed of two chloride ions and two water molecules held together by the two O—H···Cl hydrogen bonds (Table 2 and Fig. 2).

Experimental

Iron(II) chloride tetrahydrate (0.200 g, 1 mmol) was dissolved in 20 ml of acetonitrile and the solution filtered under N_2. 1.2 ml of 1-methylimidazole (6 mmol) was then added. Immediately, the colour of the solution changed from pale yellow to orange and shortly afterwards small colourless crystals of (I) began to precipitate.

Crystal data

$[Fe(C_4H_6N_2)_6]Cl_2 \cdot 2H_2O$	$Z = 2$
$M_r = 655.43$	$D_x = 1.381$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 8.0205$ (7) Å	$\mu = 0.69$ mm^{-1}
$b = 13.2884$ (12) Å	$T = 120$ (2) K
$c = 14.9438$ (14) Å	Prism, colourless
$\beta = 98.138$ (8)°	$0.26 \times 0.16 \times 0.03$ mm
$V = 1576.7$ (2) Å^3	

Data collection

Oxford Diffraction KM-4-CCD (Sapphire2 detector) diffractometer	model based on expressions derived by Clark & Reid (1998)]
ω scans	$T_{min} = 0.736$, $T_{max} = 0.901$
Absorption correction: numerical [*CrysAlis RED* (Oxford Diffraction, 2005), analytical numeric absorption correction using a multifaceted crystal	8843 measured reflections
	2736 independent reflections
	2614 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.029$
	$\theta_{max} = 25.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.9465P]$
$R[F^2 > 2\sigma(F^2)] = 0.035$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.09$	$\Delta\rho_{max} = 0.40$ e Å^{-3}
2736 reflections	$\Delta\rho_{min} = -0.28$ e Å^{-3}
198 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Selected bond lengths (Å).

Fe1—N1	2.2067 (15)	Fe1—N5	2.1864 (16)
Fe1—N3	2.2492 (15)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$A$$\cdots$Cl1^i	0.86 (3)	2.35 (3)	3.1958 (18)	171 (3)
O1—H1$B$$\cdots$Cl1	0.87 (4)	2.31 (4)	3.1708 (19)	172 (3)

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

The H atoms of the water molecule were located in a difference map and their positions and U_{iso} values were freely refined. All remaining H atoms were placed in calculated positions (C—H = 0.95–0.98 Å) and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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