

**$\mu$ -Oxo-bis{chloro[*N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine]iron(III)} diperchlorate 0.751-hydrate**Rune Kirk Egdal,<sup>a</sup> Alan Hazell<sup>b\*</sup> and Christine J. McKenzie<sup>a</sup><sup>a</sup>Department of Chemistry, University of Southern Denmark, Main Campus: Odense University, Campusvej 55, DK-5230 Odense M, Denmark, and <sup>b</sup>Department of Chemistry, Aarhus University, Langelandsgade 140, DK-8000 Århus C, Denmark

Correspondence e-mail: ach@chem.au.dk

**Key indicators**

Single-crystal X-ray study

 $T = 120$  KMean  $\sigma(\text{C}-\text{C}) = 0.003$  Å

Disorder in solvent or counterion

 $R$  factor = 0.032 $wR$  factor = 0.034

Data-to-parameter ratio = 16.2

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound,  $\mu$ -oxo-bis[bispicMe<sub>2</sub>enFeCl](ClO<sub>4</sub>)<sub>2</sub>·0.751H<sub>2</sub>O [bispicMe<sub>2</sub>en = *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine] or [Fe<sub>2</sub>Cl<sub>2</sub>O(C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>·0.751H<sub>2</sub>O, contains a complex dinuclear cation in which two Fe atoms are linked by a  $\mu$ -oxo bridge. Each Fe atom is octahedrally coordinated by the bridging O atom, four N atoms of the bispicMe<sub>2</sub>en ligand and a Cl atom. The Fe···Fe distance is 3.623 (1) Å; the Fe—O distances are 1.811 (1) and 1.814 (1) Å; the Fe—N<sub>pyridine</sub> distances vary between 2.156 (2) and 2.169 (2) Å (mean value 2.163 Å) and are considerably shorter than the Fe—N<sub>amine</sub> distances which fall into two categories, *viz.* Fe—N = 2.284 (2) and 2.296 (2) Å for the N atoms *trans* to the bridging O atom, and 2.219 (2) and 2.227 (2) Å for those *trans* to Cl. The Fe—Cl distances are 2.324 (1) and 2.334 (1) Å. The geometry is compared to that in related complexes.

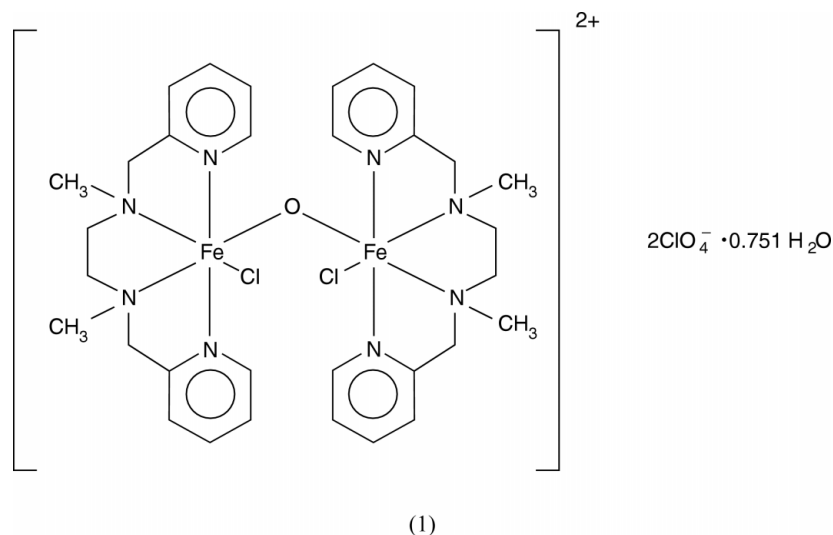
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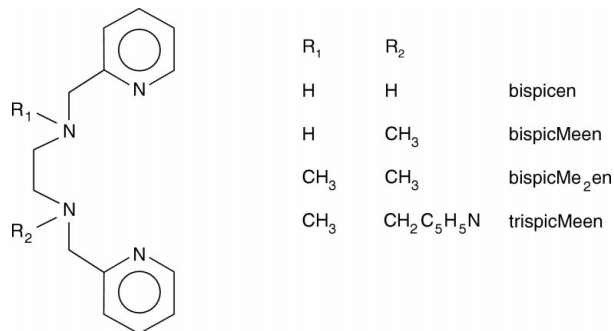
**Comment**

The structure of the title complex dinuclear cation (Fig. 1) shows that the two Fe atoms are linked by a  $\mu$ -oxo bridge;

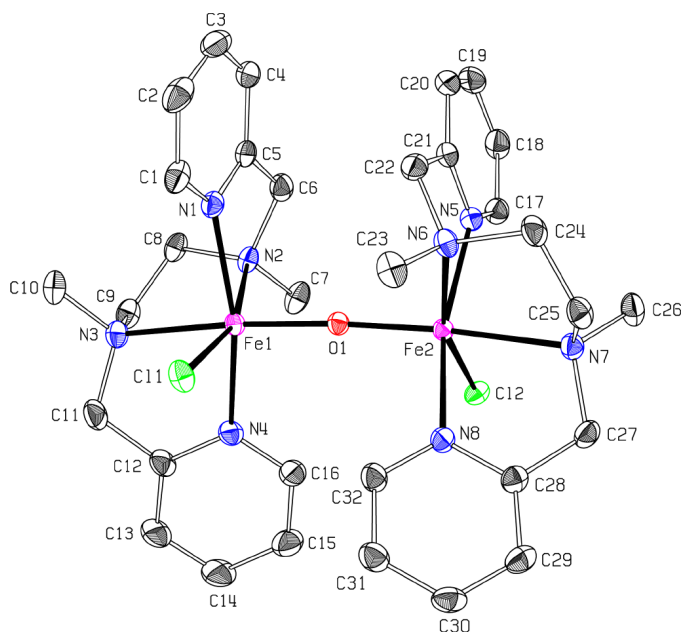


each Fe atom is octahedrally coordinated by the bridging O atom, four N atoms of the bispicMe<sub>2</sub>en ligand and a Cl atom. The Fe···Fe distance is 3.623 (1) Å; the Fe—O distances are 1.811 (1) and 1.814 (1) Å; Fe—N<sub>pyridine</sub> distances vary between 2.156 (2) and 2.169 (2) Å (mean 2.163 Å) and are considerably shorter than the Fe—N<sub>amine</sub> distances which fall into two categories, *viz.* Fe—N = 2.284 (2) and 2.296 (2) Å for the N atoms *trans* to the bridging O atom, and 2.219 (2) and

2.227 (2) Å for those *trans* to Cl. The Fe—Cl distances are 2.324 (1) and 2.334 (1) Å. These distances are similar to those found in the corresponding bispicen complex (2) (see Scheme below; Arulsamy *et al.*, 1993) and in the bispicMeen (3) and the trispicMeen (4) complexes (Nivorozhkin *et al.*, 1997). The



main differences in the geometries of these compounds are in the angle at the bridging O atom and the orientation of the ligands about the Fe—Fe axis. The Fe—O—Fe angles are 176.43 (8)° in (1), 180° in (2) (the O atom is in a special position on the inversion centre), 152.3 (3)° in (3) (the O atom is on a twofold axis) and 177.4 (7)° in (4). The Cl—Fe···Fe—Cl pseudo-torsion angles are 128.21 (2)° in (1), 180° in (2), 110.2° in (3) and 141.0° in (4).



**Figure 1**  
View of the title cation showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels; H atoms have been omitted.

The crystal packing shows the cations lying in the *ab* planes at  $z \approx 0$  or  $\frac{1}{2}$  which accounts for the crystals growing as needles parallel to the *c* axis.

The near linearity of the Fe—O—Fe angle in (1) is in agreement with the prediction based on the observed  $\nu_{\text{sym}}(\text{Fe—O—Fe})$  in the resonance-Raman spectrum (Hazell *et al.*, 1995). However, this resonance Raman result was not entirely corroborated by magnetic susceptibility measurements (Hazell *et al.*, 1995). Usually strong magnetic exchange coupling is observed for oxo-bridged diiron(III) complexes. The structural characterization now reported sheds some light on this apparent inconsistency. The Fe—O distances in (1) are significantly longer than those found in most singly bridged  $\mu$ -oxo-diiron(III) units; the mean Fe—O distance from the Cambridge Structural Database (April 2001 release; Allen & Kennard, 1993) is 1.775 Å with an s.u. of 0.001 Å, and the three longest Fe—O distances, out of 162 entries, are between 1.811 and 1.815 Å, *cf.* 1.811 and 1.814 Å found for (1). Thus, a markedly weaker exchange coupling for this particular group is consistent with the observed geometry. The electronegative chloride ions *cis* to the  $\mu$ -oxo group and the Cl—Fe···Fe—Cl pseudo-torsion angle will influence the Fe—O bond length and consequent overlap integral of the magnetic orbitals.

## Experimental

Red crystals of the title compound (1) were prepared by the method described by Hazell *et al.* (1995).

### Crystal data

[Fe<sub>2</sub>Cl<sub>2</sub>O(C<sub>16</sub>H<sub>22</sub>N<sub>4</sub>)<sub>2</sub>]  
(ClO<sub>4</sub>)<sub>2</sub>·0.751H<sub>2</sub>O  
*M<sub>r</sub>* = 951.83  
Monoclinic, *P*<sub>2</sub><sub>1</sub>/*c*  
*a* = 13.632 (3) Å  
*b* = 17.956 (4) Å  
*c* = 16.489 (3) Å  
 $\beta$  = 94.938 (4)°  
*V* = 4021 (1) Å<sup>3</sup>  
*Z* = 4

*D<sub>x</sub>* = 1.572 Mg m<sup>-3</sup>  
Mo *K*α radiation  
Cell parameters from 8666 reflections  
 $\theta$  = 2.3–30.5°  
 $\mu$  = 1.05 mm<sup>-1</sup>  
*T* = 120 K  
Needle, red  
0.50 × 0.13 × 0.12 mm

### Data collection

Siemens SMART CCD diffractometer  
 $\omega$  rotation scans with narrow frames  
Absorption correction: by integration (*XPREP*; Siemens, 1995)  
*T<sub>min</sub>* = 0.647, *T<sub>max</sub>* = 0.899  
45 381 measured reflections

12 123 independent reflections  
8461 reflections with  $I > 3\sigma(I)$   
*R<sub>int</sub>* = 0.042  
 $\theta_{\text{max}}$  = 30.5°  
*h* = -19 → 18  
*k* = -25 → 24  
*l* = -22 → 23

### Refinement

Refinement on *F*  
*R* = 0.032  
*wR* = 0.034  
*S* = 0.88  
8461 reflections  
521 parameters

H-atom parameters constrained  
 $w = 1/[\sigma_{\text{cs}}(F^2) + 0.1 + 1.03F^2]^{1/2}$   
 $(\Delta/\sigma)_{\text{max}}$  = 0.001  
 $\Delta\rho_{\text{max}}$  = 0.72 (8) e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}}$  = -0.51 (8) e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Fe1—Fe2	3.623 (1)	Fe2—Cl2	2.334 (1)
Fe1—Cl1	2.324 (1)	Fe2—O1	1.811 (1)
Fe1—O1	1.814 (1)	Fe2—N5	2.169 (2)
Fe1—N1	2.161 (2)	Fe2—N6	2.227 (2)
Fe1—N2	2.219 (2)	Fe2—N7	2.284 (2)
Fe1—N3	2.296 (2)	Fe2—N8	2.164 (2)
Fe1—N4	2.156 (2)		
O1—Fe1—N1	96.59 (6)	O1—Fe2—N6	93.51 (6)
O1—Fe1—N2	92.93 (6)	O1—Fe2—N7	165.92 (6)
O1—Fe1—N3	166.23 (6)	O1—Fe2—N8	95.58 (6)
O1—Fe1—N4	96.91 (6)	O1—Fe2—Cl2	101.56 (4)
O1—Fe1—Cl1	102.00 (4)	N5—Fe2—N6	74.92 (6)
N1—Fe1—N2	75.42 (6)	N5—Fe2—N7	91.71 (6)
N1—Fe1—N3	91.48 (6)	N5—Fe2—N8	164.83 (6)
N1—Fe1—N4	164.24 (6)	N5—Fe2—Cl2	92.15 (5)
N1—Fe1—Cl1	93.19 (5)	N6—Fe2—N7	78.71 (6)
N2—Fe1—N3	78.29 (6)	N6—Fe2—N8	96.87 (6)
N2—Fe1—N4	95.80 (6)	N6—Fe2—Cl2	161.39 (4)
N2—Fe1—Cl1	162.25 (4)	N7—Fe2—N8	73.99 (6)
N3—Fe1—N4	73.75 (6)	N7—Fe2—Cl2	88.54 (4)
N3—Fe1—Cl1	88.62 (4)	N8—Fe2—Cl2	92.50 (5)
N4—Fe1—Cl1	91.92 (5)	Fe1—O1—Fe2	176.43 (8)
O1—Fe2—N5	97.62 (6)		
Cl1—Fe1—Fe2—Cl2	128.21 (2)		

**Table 2**

Hydrogen-bonding 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>
O10—HO10 <i>a</i> ···O6 <i>a</i>	0.91	1.87	2.768 (3)	167
O10—HO10 <i>a</i> ···O6 <i>b</i>	0.91	2.08	2.976 (4)	168
O10—HO10 <i>b</i> ···O3	0.91	2.02	2.935 (3)	176

The H atoms of the ligand were constrained to have C—H = 0.95 Å and  $U_{iso} = 1.2U_{eq}$  of the atom to which they are attached. The H atoms of the water molecule O10 were obtained from a difference

map and kept fixed. One of the perchlorate ions (with the central Cl4 atom) was disordered, appearing in the Fourier map as a very anisotropic heavy atom surrounded by six light atoms, and was modelled as two interpenetrating perchlorate ions which were constrained to have regular tetrahedral geometry with all Cl—O distances the same. Site-occupation factors for the two ions were set, arbitrarily, to be 0.5. The site-occupation factor for the water molecule was refined and found to be 0.751 (5).

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEP* (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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