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Key indicators

Single-crystal X-ray study  
 T = 213 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$   
 Disorder in main residue  
 R factor = 0.047  
 wR factor = 0.131  
 Data-to-parameter ratio = 13.2

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

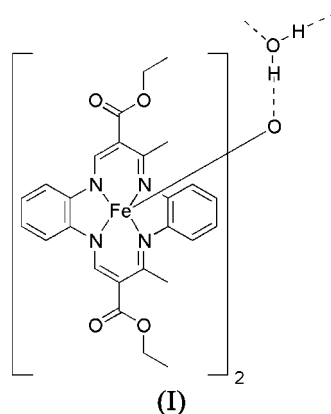
$\mu$ -Oxo-bis[(diethyl 6,17-dimethyldibenzo-  
 [a,h]-5,9,14,18-tetraaza[14]annulene-  
 7,16-dicarboxylato)iron(III)] sesquihydrate

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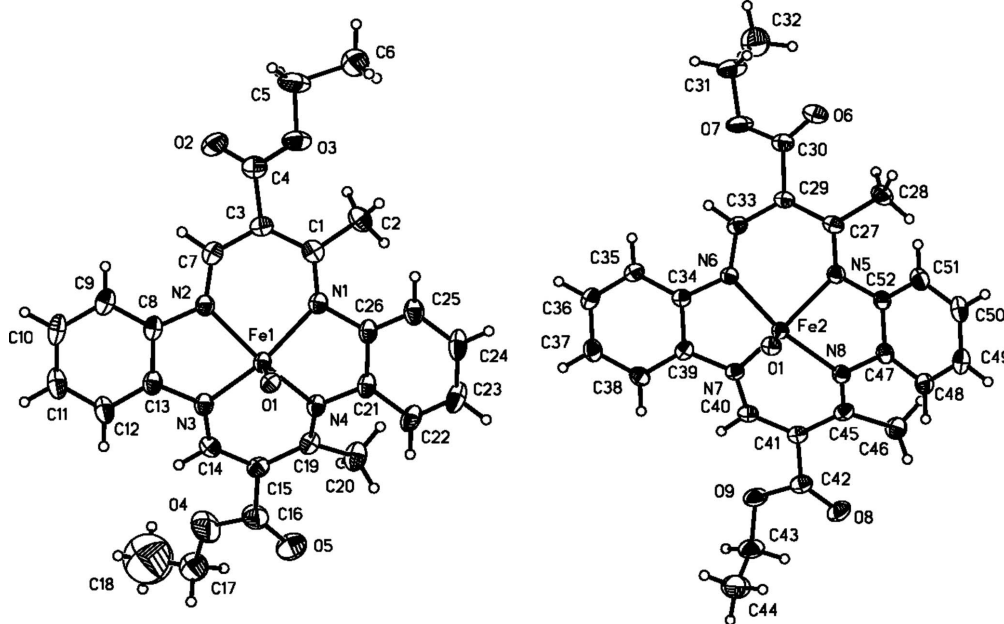
The title compound (systematic name:  $\mu$ -oxo-bis{[4,15-bis-(ethoxycarbonyl)-5,14-dimethyl-2,7,13,17-tetraazatricyclo-[16.4.0.0<sup>7,12</sup>]docosa-3,5,7,9,11,13,15,18(1),19,21-decaene-2,17-diido]iron(III)} sesquihydrate),  $[\text{Fe}_2(\text{C}_{26}\text{H}_{26}\text{N}_4\text{O}_4)\text{O}]\cdot 1.5\text{H}_2\text{O}$ , crystallizes in the monoclinic space group  $C2/c$  and has two iron centres which are coordinated by macrocyclic ligands with an  $\text{N}_4$  donor set. These iron centres are bridged by a  $\mu$ -oxo ligand, resulting in the formation of a dinuclear complex unit. The  $\mu$ -oxo ligand interacts with a water molecule *via* strong hydrogen bonds. These solvent molecules aggregate by additional hydrogen bonds, producing a tetranuclear aggregate. Towards the outer rim of the cavity formed by the carboxyethyl substituents attached to the tetraaza-annulene systems there are additional solvent molecules. Due to much weaker hydrogen-bond interactions, the latter are disordered and have site-occupancy factors less than 1.

Comment

Our interest in the title compound, (I), arises from the fact that this complex shows an outstanding catalytic potential in the oxidase-like oxidation of hydroquinone to *p*-benzoquinone under atmospheric pressure of  $\text{O}_2$ . In acetonitrile containing a small amount of water, the title compound is nearly two orders of magnitude more active than any other complex we have investigated, including substantial variation of the transition metals, the ligand backbone and the substitution pattern of the ligands (Knaudt, 1998; Jäger *et al.*, 1996). The synthesis and the spectroscopic and analytical data of the parent iron(II) complex of (I) (Müller *et al.*, 1989), the structure of the free ligand (Görls *et al.*, 1990) and the structures of several iron(II/III) derivatives (Weber *et al.*, 2002, 2005; Käpplinger *et al.*, 1999) have already been published.



The scheme shows the constitutional formula of the coordination of one of the Fe atoms of the dinuclear complex



**Figure 1**

The molecular structure of the coordination mode of Fe1 (left) and Fe2 (right). The bridging oxygen atom (O1) is shown in both units. Displacement ellipsoids are drawn at the 40% probability level.

unit. The molecular structure is presented in Fig. 1 in which, for the sake of clarity, the two coordination environments of the Fe atoms are depicted separately. The most important bond lengths and angles are given in Table 1. It can be seen that the coordination around each Fe atom is distorted square-pyramidal, with the Fe atoms situated above the base of the square pyramid represented by the four N atoms. The distances from the basal plane of the pyramid to the Fe atoms are 0.672 (2) (Fe1) and 0.682 (1) Å (Fe2). The observed Fe—O distances are 1.784 (2) (Fe1—O1) and 1.788 (2) Å (Fe2—O1). These distances correspond very well with the Fe—O bond lengths in other structurally characterized  $\mu$ -oxo-bridged dinuclear iron complexes in which the iron centres are also coordinated by macrocyclic ligands with an  $N_4$  donor set. A search of the Cambridge Structural Database (Version 5.26 of November 2004; Allen, 2002) found 36 structurally characterized  $\mu$ -oxo-bridged dinuclear iron compounds in which the remaining coordination sites around the Fe atoms are occupied by a macrocyclic  $N_4$  donor ligand. The ligand systems are generally similar to naturally occurring ligands such as porphyrin, porphycene, phthalocyanine or corrole (for the most recent examples, see Hayashi *et al.*, 2003; Cheng *et al.*, 2004; Litvinov *et al.*, 2003; Chang *et al.*, 2004; Lee *et al.*, 2003; Baba *et al.*, 2004; Ercolani *et al.*, 1983; Simkhovich *et al.*, 2001). In general, the corresponding bond lengths in  $\mu$ -hydroxo-bridged compounds are significantly longer [1.821 (8)–1.952 (2) Å; Scheidt *et al.*, 1992; Evans *et al.*, 1997].

The most outstanding structural characteristic of the title compound is the Fe1—O1—Fe2 angle of 133.0 (1)°, which represents the most bent arrangement observed in  $\mu$ -oxo-diiron complexes to date; these are commonly 150–180°. There are only two examples with bond angles below 150°. One of them is a porphycene derivative (Lausmann *et al.*, 1994) with

an Fe—O—Fe angle of 145.3 (2)°. The other is the complex reported by Weiss & Goedken (1979), which is closely related to the title compound in that the substitution pattern of the ligand backbone is Me/H/Me instead of Me/CO<sub>2</sub>Et/H. The corresponding bond angle is observed to be 142.75 (9)°. Another interesting feature which, together with the tight Fe—O—Fe angle, determines the supramolecular structure of the title compound is the fact that the carbonyl groups of the carboxyethyl substituents show a *trans* arrangement in the ligand coordinating Fe1, whereas they are *cis* configured in the ligand bound to Fe2.

The supramolecular structure of the title compound is realised by the incorporation of solvent water molecules. Fig. 2 shows that the O atom bridging the two Fe atoms forms a hydrogen bond [O1...O10 = 2.887 (6) Å]. The very small Fe—O—Fe angle is obviously a crucial prerequisite for the formation of this hydrogen bond, which is otherwise not possible for steric reasons. The solvent molecule shows an additional interaction with carbonyl atom O5 which is slightly weaker [O5...O10 = 3.193 (7) Å]. A centrosymmetric tetranuclear supramolecular arrangement of complex units is formed by the hydrogen bonding of O10 to a symmetry equivalent [O10...O10A<sup>i</sup> = 2.957 (6) Å; symmetry code: (i) 1 - x, y,  $\frac{1}{2}$  - z].

Fig. 3 presents another view of the tetranuclear supramolecular aggregate in which it can be seen that the *trans* configuration of the carbonyl groups (O5 and O2, *cf.* Fig. 1), together with the small bond angle at the bridging O atom, leads to the formation of a cavity, allowing the incorporation of atoms O10 and O10A *via* strong hydrogen bonds as well as additional water molecules towards the outer rim of the cavity. These water molecules, interacting also with atoms O10, O10A, O5 and O5A, are much less efficiently bound, resulting

in a rather diffuse and disordered arrangement with site-occupancy factors less than 1.

**Experimental**

The synthesis of the title compound, together with the corresponding spectroscopic and analytical data, have been published elsewhere (Müller *et al.*, 1989). Crystals of the title compound were isolated from a saturated solution of the parent iron(II) complex in 15 ml acetonitrile containing 15 µl water after oxidation by air.

*Crystal data*

[Fe<sub>2</sub>(C<sub>26</sub>H<sub>26</sub>N<sub>4</sub>O<sub>4</sub>)O]·1.5H<sub>2</sub>O  
*M<sub>r</sub>* = 1071.74  
 Monoclinic, *C2/c*  
*a* = 27.322 (6) Å  
*b* = 13.494 (4) Å  
*c* = 29.838 (5) Å  
 $\beta$  = 111.26 (2)°  
*V* = 10252 (4) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.385 Mg m<sup>-3</sup>  
 Mo *K*α radiation  
 Cell parameters from 25 reflections  
 $\theta$  = 20.1–27.8°  
 $\mu$  = 0.63 mm<sup>-1</sup>  
*T* = 213 (2) K  
 Block, red  
 0.6 × 0.4 × 0.3 mm

*Data collection*

Enraf–Nonius CAD-4 diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction:  $\psi$  scan (North *et al.*, 1968)  
*T<sub>min</sub>* = 0.776, *T<sub>max</sub>* = 0.830  
 9161 measured reflections  
 8963 independent reflections  
 6718 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.024  
 $\theta_{max}$  = 25.0°  
*h* = 0 → 32  
*k* = -16 → 0  
*l* = -35 → 33  
 3 standard reflections  
 frequency: 60 min  
 intensity decay: 3.6%

*Refinement*

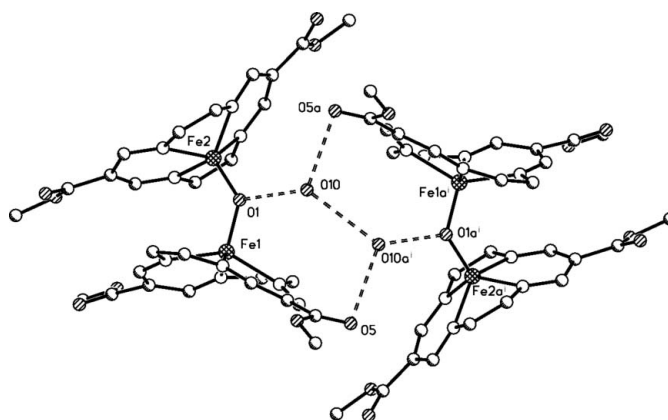
Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.047  
*wR*(*F*<sup>2</sup>) = 0.131  
*S* = 1.09  
 8963 reflections  
 681 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 35.0302P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.004$   
 $\Delta\rho_{max} = 0.74 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.52 \text{ e \AA}^{-3}$

**Table 1**

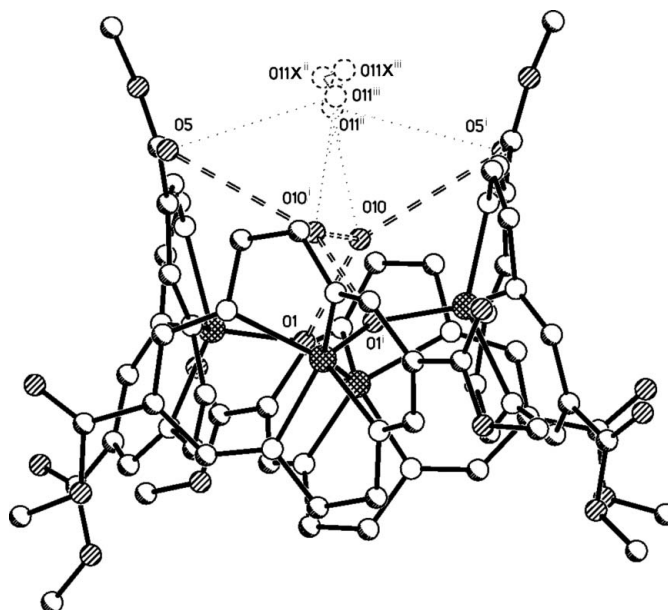
Selected geometric parameters (Å, °).

Fe1–O1	1.784 (2)	Fe2–O1	1.788 (2)
Fe1–N3	2.020 (3)	Fe2–N7	2.022 (3)
Fe1–N2	2.023 (3)	Fe2–N6	2.026 (3)
Fe1–N4	2.038 (3)	Fe2–N8	2.043 (3)
Fe1–N1	2.045 (3)	Fe2–N5	2.044 (3)
O1–Fe1–N3	112.13 (12)	O1–Fe2–N6	111.34 (11)
O1–Fe1–N2	112.42 (11)	N7–Fe2–N6	78.50 (11)
N3–Fe1–N2	78.82 (12)	O1–Fe2–N8	107.00 (11)
O1–Fe1–N4	106.88 (11)	N7–Fe2–N8	87.49 (11)
N3–Fe1–N4	87.00 (12)	N6–Fe2–N8	141.63 (11)
N2–Fe1–N4	140.70 (12)	O1–Fe2–N5	105.92 (11)
O1–Fe1–N1	105.93 (12)	N7–Fe2–N5	139.93 (11)
N3–Fe1–N1	141.93 (12)	N6–Fe2–N5	87.27 (11)
N2–Fe1–N1	87.56 (12)	N8–Fe2–N5	80.85 (11)
N4–Fe1–N1	81.42 (12)	Fe1–O1–Fe2	133.01 (14)
O1–Fe2–N7	114.15 (11)	C47–C52–N5	116.2 (3)

The H atoms of the hydrate molecules were not located. All other H atoms were placed in idealized positions, with C–H = 0.93–0.97 Å, and a single isotropic displacement parameter was refined for each group of H atoms bound to a common parent atom. Disorder treatment: C6 and the corresponding H atoms, site-occupancy factor (sof)



**Figure 2**  
 Aggregation of two dinuclear complex subunits *via* hydrogen-bond (dashed lines) interactions with solvent water molecules. H atoms, phenylene bridges and methyl substituents have been omitted for clarity [symmetry code: (i) 1 - *x*, *y*,  $\frac{1}{2}$  - *z*].



**Figure 3**  
 Side view of the tetranuclear supramolecular aggregate, showing the cavity for the water molecules [symmetry codes: (i) 1 - *x*, *y*,  $\frac{1}{2}$  - *z*; (ii) *x*, 1 + *y*, *z*; (iii) 1 - *x*, 1 + *y*,  $\frac{1}{2}$  - *z*].

= 0.46 (3); C6X, sof = 0.54 (3); C32 and the corresponding H atoms, sof = 0.54 (1), C32X, sof = 0.46 (1); the sofs for C17, C18 and the corresponding H atoms have been fixed to 0.33 to produce reasonable displacement parameters; the sofs for C17X and C18X were therefore fixed at 0.67.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* (Boer *et al.*, 1984); data reduction: *MolEN* (Nonius, 1990); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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