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μ-Oxo-bis[(protoporphyrin IX dimethyl ester)-iron(III)]

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In the title compound, $[Fe_2(C_{36}H_{36}N_4O_4)_2O]$, the Fe—O—Fe bond angle is 170.5 (2)° and the two porphyrin rings are twisted by 27.2 (4)° with respect to each other.

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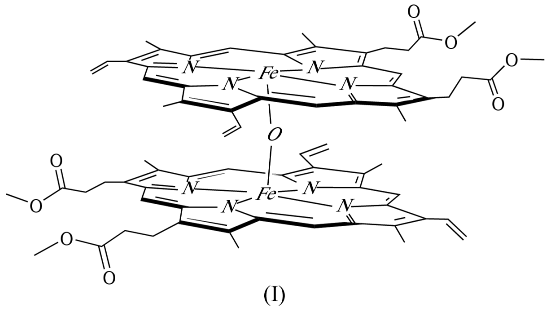
Key indicators

Single-crystal X-ray study
T = 133 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
R factor = 0.067
wR factor = 0.216
Data-to-parameter ratio = 12.4

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

Comment

The μ-oxo dimer of iron protoporphyrin IX (FePPIX) is relevant in biology. For example, the black pigment of *Porphyromonas gingivalis*, a principal agent in adult periodontitis, has been identified as the μ-oxo dimer of FePPIX (Smalley *et al.*, 1998, 2004). Furthermore, the antimalarial drug chloroquine and its analogues have been shown to interact with the μ-oxo dimer of FePPIX *via* non-covalent π–π stacking between the quinolinal moieties and the porphyrin rings of the μ-oxo dimer (Dorn *et al.*, 1998; Leed *et al.*, 2002; Moreau *et al.*, 1982; Vippagunta *et al.*, 1999; Vippagunta *et al.*, 2000), although the exact stoichiometry may vary depending on the experimental conditions employed (Leed *et al.*, 2002).



(I)

Importantly, aqueous solutions of FePPIX at pH > 7.0 contain the μ-oxo dimer as the dominant species (Silver & Lukas, 1983), and this μ-oxo dimer has also been shown to

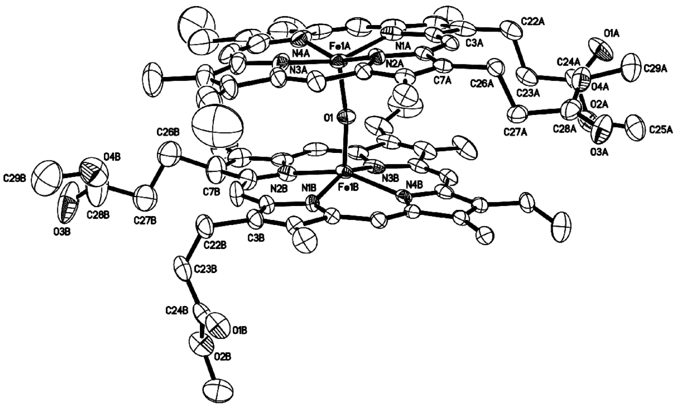


Figure 1
Perspective view of the title compound, highlighting the μ-O bridge, with displacement ellipsoids drawn at the 35% probability level. H and lower occupancy disordered atoms have been omitted for clarity.

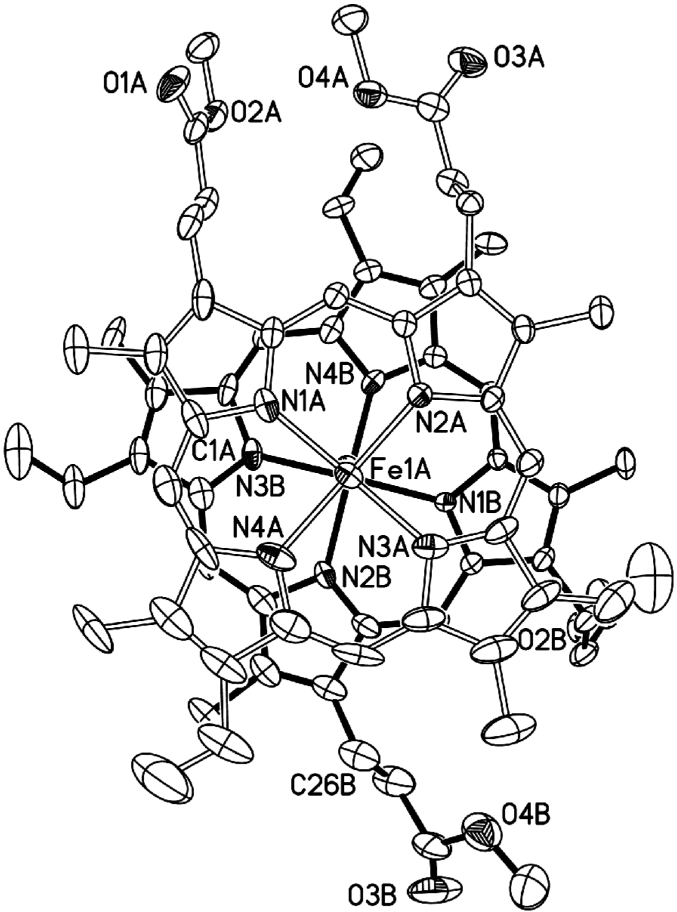


Figure 2
Perspective view of the title compound, highlighting the relative orientation of the porphyrin rings, with displacement ellipsoids drawn at the 30% probability level. H and lower occupancy disordered atoms have been omitted for clarity.

form adducts with ligands such as histidine and histamine (Medhi & Silver, 1989). We have successfully crystallized a soluble analogue of the μ-oxo dimer of FePPIX, namely that of the dimethyl ester, *i.e.* [FePPIXDME]$_2$(μ-O), (I). To the best of our knowledge, although several μ-oxo dimer compounds of iron porphyrins are known (Cheng *et al.*, 1998, and references therein; Li *et al.*, 2000; Scheidt, 2000), X-ray structural data for (I) have not been reported, although very brief mention of the structure has appeared (Anderson *et al.*, 1982). In this paper, we report a high quality single-crystal X-ray structure of (I).

The molecular structure of (I) is shown in Fig. 1 and selected geometric parameters are collected in Table 1. One of the ester groups (C26*B*–C29*B*) of the porphyrin associated with Fe1*B* is disordered over two sites, with occupancies of 0.563 (8) and 0.437 (8); the major component is shown in Fig. 1. The two porphyrin rings show a twist with respect to each other, *viz.* 27.4 (2)°. The ester pair on one porphyrin macrocycle is situated away from the ester pair of the other porphyrin macrocycle, presumably due to the steric hindrance caused by the presence of the bulky ester groups. The porphyrin core associated with Fe1*A* is somewhat domed and that associated with Fe1*B* is moderately saddled. The Fe—O—Fe oxo bridge is slightly non-linear with a bond angle of 170.5 (2)°. A projection down the Fe—O—Fe axis is shown in Fig. 2.

Experimental

The title compound was purchased from Midcentury Chemicals. Single crystals were obtained by room temperature evaporation of a dichloromethane–heptane solution of the compound in air.

Crystal data

[Fe$_2$(C$_{36}$H$_{36}$N$_4$O$_4$)$_2$O]
M_r = 1305.08
Triclinic, $P\overline{1}$
a = 8.9496 (6) Å
b = 15.1684 (12) Å
c = 24.860 (2) Å
α = 107.509 (2)°
β = 91.601 (2)°
γ = 100.455 (2)°
V = 3152.7 (4) Å^3
Z = 2
D_x = 1.375 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6348 reflections
θ = 2.5–25.0°
μ = 0.53 mm^{-1}
T = 133 (2) K
Prism, black
0.42 × 0.22 × 0.20 mm

Data collection

Bruker SMART/*P*4 diffractometer
φ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2000)
$T_{\min}$ = 0.809, $T_{\max}$ = 0.902
35132 measured reflections
10870 independent reflections
6685 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.057
$\theta_{\max}$ = 25.0°
$h = -10 \rightarrow 10$
$k = -18 \rightarrow 18$
$l = -29 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.067
$wR(F^2)$ = 0.216
S = 1.05
10870 reflections
875 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.14P)^2 + 1.54P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.012
$\Delta\rho_{\max}$ = 0.82 e Å^{-3}
$\Delta\rho_{\min}$ = −0.73 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1*A*—O1	1.748 (3)	O1—Fe1*B*	1.748 (3)
Fe1*A*—N3*A*	2.065 (5)	Fe1*B*—N2*B*	2.062 (4)
Fe1*A*—N2*A*	2.067 (4)	Fe1*B*—N1*B*	2.068 (4)
Fe1*A*—N1*A*	2.087 (5)	Fe1*B*—N3*B*	2.077 (4)
Fe1*A*—N4*A*	2.091 (5)	Fe1*B*—N4*B*	2.097 (4)
O1—Fe1*A*—N3*A*	102.35 (16)	O1—Fe1*B*—N2*B*	102.49 (16)
O1—Fe1*A*—N2*A*	100.60 (15)	O1—Fe1*B*—N1*B*	102.23 (15)
N3*A*—Fe1*A*—N2*A*	87.54 (17)	N2*B*—Fe1*B*—N1*B*	87.96 (15)
O1—Fe1*A*—N1*A*	100.18 (16)	O1—Fe1*B*—N3*B*	100.98 (15)
N3*A*—Fe1*A*—N1*A*	157.46 (17)	N2*B*—Fe1*B*—N3*B*	88.04 (18)
N2*A*—Fe1*A*—N1*A*	88.15 (16)	N1*B*—Fe1*B*—N3*B*	156.77 (16)
O1—Fe1*A*—N4*A*	102.41 (17)	O1—Fe1*B*—N4*B*	101.26 (15)
N3*A*—Fe1*A*—N4*A*	89.0 (2)	N2*B*—Fe1*B*—N4*B*	156.25 (16)
N2*A*—Fe1*A*—N4*A*	156.93 (17)	N1*B*—Fe1*B*—N4*B*	87.15 (15)
N1*A*—Fe1*A*—N4*A*	86.3 (2)	N3*B*—Fe1*B*—N4*B*	87.35 (17)
Fe1*A*—O1—Fe1*B*	170.5 (2)		

H atoms were constrained in the riding model approximation, fixed to their parent C atoms, with C—H distances set to 0.95, 0.99 and 0.98 Å for sp^2, CH$_2$ and CH$_3$ H atoms, respectively and with $U_{\rm iso}$ values set at 1.2$U_{\rm eq}$, 1.2$U_{\rm eq}$ and 1.5$U_{\rm eq}$ of the parent C atom, respectively.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT* and *SHELXTL* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick,

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1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHEXLTL*.

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