

μ -Oxo-bis{[(6-hydroxymethyl-2-pyridylmethyl)bis(2-pyridylmethyl)amine- $\kappa^5 N, N', N'', N''', O$]iron(III)} tetrakis(perchlorate)

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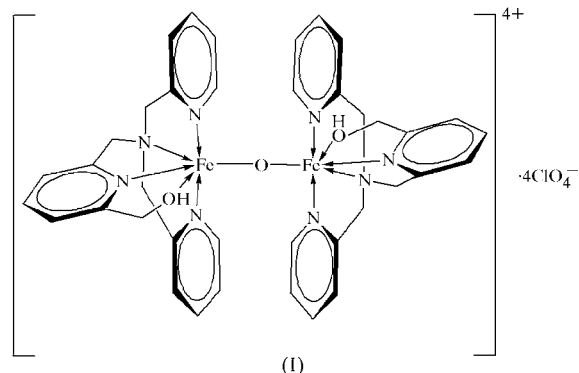
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The novel μ -oxo-diiron complex $[\text{Fe}_2\text{O}(\text{BPHPA})_2](\text{ClO}_4)_4$ [BPHPA is (6-hydroxymethyl-2-pyridylmethyl)bis(2-pyridylmethyl)amine, $\text{C}_{19}\text{H}_{20}\text{N}_4\text{O}$], contains a binuclear centrosymmetric $[\text{Fe}_2\text{O}(\text{BPHPA})_2]^{4+}$ cation (the bridging O atom lies on an inversion centre) and four perchlorate anions. Each iron ion is coordinated by four N atoms [$\text{Fe}-\text{N} = 2.117(5)$ – $2.196(5)$ Å] and one O atom [$\text{Fe}-\text{O} = 2.052(5)$ Å] from a BPHPA ligand, and by one bridging oxo atom [$\text{Fe}-\text{O} = 1.7896(9)$ Å], forming a distorted octahedron. There are hydrogen bonds between the hydroxy group and perchlorate O atoms [$\text{O}-\text{H}\cdots\text{O} = 2.654(7)$ Å].

Comment

TPA [tris(2-pyridylmethyl)amine] is a versatile tetradentate ligand which forms stable complexes with a large number of transition metal ions (Gultneh *et al.*, 2003; Jitsukawa *et al.*, 2001; Mandon *et al.*, 2002; Zhang *et al.*, 2003); in particular, μ -oxo-diiron(III)-TPA complexes mimic the structure of non-heme diiron proteins, such as monooxygenase (Feig & Lippard, 1994). Besides the μ -oxo atom, these complexes often have one or two additional oxoanionic bridges (carboxylate or phosphate) or are coordinated by other small molecules (*e.g.* water) (Dong *et al.*, 1995; Kojima *et al.*, 1993; Norman, Yan *et al.*, 1990). While only one μ -oxo-diiron(III)-TPA complex coordinated with a pentadentate TPA ligand and one bridging oxo atom has been reported (Lange *et al.*, 1999), it is interesting to design more of these pentadentate TPA ligands in order to obtain μ -oxo-diiron(III)-TPA complexes that may significantly affect the catalytic oxidation reaction. We have obtained a novel dinuclear iron(III)-oxo-TPA complex, *viz.* $[\text{Fe}_2\text{O}(\text{BPHPA})_2](\text{ClO}_4)_4$, (I), with a pentadentate TPA ligand substituted by a hydroxymethyl group in the α position [BPHPA is (6-hydroxymethyl-2-

pyridylmethyl)bis(2-pyridylmethyl)amine]. We report here the synthesis, crystal structure, spectroscopic properties and H_2O_2 dismutation activity of (I).



The crystal structure of (I) is composed of a dinuclear $[\text{Fe}_2\text{O}(\text{BPHPA})_2]^{4+}$ cation and four perchlorate anions, as illustrated in Fig. 1.

This μ -oxo dimer has a linear $\text{Fe}-\text{O}-\text{Fe}$ structure, because the bridging O atom lies on an inversion centre. The geometry at each iron cation is distorted octahedral, with *trans* ligand chelating angles of less than 180° (Table 1). The flexibility of the TPA ligand is illustrated by the fact that there are five angles smaller than 90° and two angles larger than 90° . The lengths of the $\text{Fe}-\text{N}$ bonds range from 2.117 (5) to 2.196 (5) Å, the $\text{Fe}-\text{O}_{\text{OH}}$ distance is 2.052 (5) Å and the $\text{Fe}-\text{O}_{\text{oxo}}$ distance is 1.7896 (9) Å.

The $\text{Fe}-\text{O}_{\text{oxo}}$ bond distance in (I) is similar to the corresponding bond distance [1.789 (1) Å] in $[\text{Fe}_2(\mu\text{-O})(6\text{-C}_6\text{H}_4\text{O-TPA})_2(\text{BPh}_4)_2]$, (II) (Lange *et al.*, 1999), which is the only published structure of a μ -oxo-diiron(III)-TPA complex coordinated by five atoms of a substituted TPA ligand and one oxo bridge; in (II), the TPA ligand is substituted by one phenol

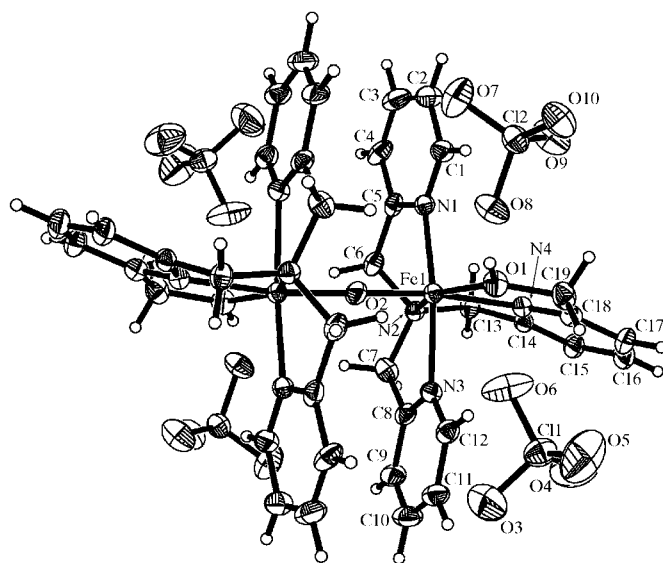
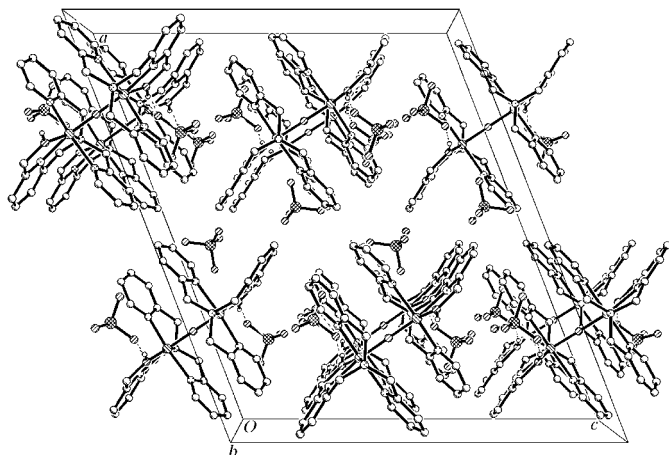


Figure 1

A view of (I), shown with 30% probability displacement ellipsoids. Unlabelled atoms were generated by the symmetry code $(\frac{1}{2} - x, \frac{3}{2} - y, -z)$.


Figure 2

A packing diagram of (I). H atoms not involved in hydrogen bonding have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

group in the α position of a pyridine (py) ring. However, the Fe–N_{amine} distance [2.196 (5) Å] and the mean Fe–N_{py} distance (2.128 Å) in (I) are both shorter than the equivalent distances in the structure of (II) (by 0.014 and 0.039 Å, respectively). Hydrogen bonds exist between the OH group of the hydroxymethyl group and an O atom of a perchlorate anion [O1–H···O8 = 2.654 (7) Å; Table 2], as shown in the packing diagram (Fig. 2).

The IR spectra of the diiron complex and the ligand show typical aromatic and aliphatic bands. The coordination of the pyridine moieties causes a shift of the aromatic C=N bands to higher wavenumbers. Two strong new bands in the spectrum of the diiron complex can be assigned to the $\nu(\text{Cl–O})$ bands of ClO₄ at 1089 and 622 cm⁻¹. The presence of the Fe–O–Fe linkage is also confirmed by the appearance of the $\nu(\text{Fe–O–Fe})$ band at 833 cm⁻¹ (Chen *et al.*, 2001).

The intense peak in the UV range is slightly blue-shifted compared with that in the free ligand (from 262 to 252 nm) and is assigned to a ligand-centred $\pi\text{--}\pi^*$ transition. Upon metallation of the ligand, four peaks appear at 323, 358, 487 and 658 nm, which are assigned to oxo-to-Fe^{III} ligand-to-metal charge-transfer transitions (Norman, Holz *et al.*, 1990).

The diiron-oxo complex also shows H₂O₂ dismutation activity in acetonitrile with a complex (1 mM)/H₂O₂ ratio of 1:1000 at 298 K. The turnover of the reaction for the first 20 min is 188; however, the complex has no catalytic activity for the oxidation of cyclohexane or cyclohexene. Further studies of the reactive mechanism are in progress.

Experimental

To a solution of the BPHPA ligand [prepared as described by He *et al.* (2000)] (0.006 g, 0.187 mol) in methanol (2 ml) was added a solution of Fe(ClO₄)₃·9H₂O (0.097 g, 0.187 mmol) in methanol (2 ml). The resulting solution was stirred for 20 min and diethyl ether was added dropwise until a solid precipitated completely; the precipitate was then collected by filtration and dried *in vacuo* (yield: 0.063 g, 58%). The complex was redissolved in acetonitrile and left to stand at room temperature for a week, yielding red crystals. ESI-MS: *m/z*

[[BPHPAFe]₂O] + ClO₄ – 2H]⁺ 865, [[(BPHPAFe)₂O] – 2H]²⁺ 383; IR (KBr, cm⁻¹): 3434 (*m*), 3079 (*w*), 2927 (*w*), 1606 (*s*), 1581 (*w*), 1484 (*m*), 1444 (*s*), 1349 (*w*), 1311 (*w*), 1288 (*w*), 1089 (*s*, ClO₄), 1025 (*s*), 902 (*w*), 881 (*w*), 833 (*s*, Fe–O–Fe), 765 (*s*), 734 (*w*), 649 (*w*), 622 (*s*, ClO₄), 532 (*w*); UV λ_{max} , nm (ϵ_{max} , M⁻¹, cm⁻¹): 252 (2.8 × 10⁴), 323 (1.0 × 10⁴), 358 (8.5 × 10³), 487 (613), 658 (178).

Crystal data

[Fe₂O(C₁₉H₂₀N₄O)₂](ClO₄)₄
M_r = 1166.28
 Monoclinic, *C2/c*
a = 24.0733 (9) Å
b = 9.9223 (3) Å
c = 20.5055 (8) Å
 β = 111.220 (2)°
V = 4565.9 (3) Å³
Z = 4

D_x = 1.697 Mg m⁻³
 Mo K α radiation
 Cell parameters from 3348 reflections
 θ = 1.8–25.1°
 μ = 0.96 mm⁻¹
T = 293 (2) K
 Block, red
 0.34 × 0.28 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
T_{min} = 0.713, *T_{max}* = 0.856
 7191 measured reflections

4002 independent reflections
 3000 reflections with *I* > 2 σ (*I*)
R_{int} = 0.045
 θ_{max} = 25.1°
h = –28 → 25
k = –11 → 11
l = –12 → 24

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.075
wR(*F*²) = 0.191
S = 1.09
 4002 reflections
 326 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 58.9568P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.66 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.48 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Fe1–O2	1.7896 (9)	Fe1–N4	2.132 (5)
Fe1–O1	2.052 (5)	Fe1–N3	2.134 (5)
Fe1–N1	2.117 (5)	Fe1–N2	2.196 (5)
O2–Fe1–O1	105.26 (15)	N1–Fe1–N3	155.3 (2)
O2–Fe1–N1	94.12 (14)	N4–Fe1–N3	82.7 (2)
O1–Fe1–N1	105.2 (2)	O2–Fe1–N2	102.90 (14)
O2–Fe1–N4	172.06 (15)	O1–Fe1–N2	151.4 (2)
O1–Fe1–N4	73.8 (2)	N1–Fe1–N2	77.1 (2)
N1–Fe1–N4	93.7 (2)	N4–Fe1–N2	77.6 (2)
O2–Fe1–N3	89.61 (14)	N3–Fe1–N2	78.3 (2)
O1–Fe1–N3	97.2 (2)	Fe1–O2–Fe1 ⁱ	180

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

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>
O1–H20···O8	0.84 (6)	1.82 (3)	2.654 (7)	169 (8)

H atoms bonded to C atoms were placed at calculated positions, with C–H distances of 0.93 and 0.97 Å, and treated as riding atoms. The H atom of the hydroxy group was located from a difference map and refined isotropically, with an O–H distance restraint of 0.85 Å.

Data collection: SMART (Siemens, 1996); cell refinement: SMART and SAINT (Siemens, 1994); data reduction: SAINT and XPREP in

SHELXTL (Siemens, 1994); program(s) used to solve structure: *SHELXTL*; program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1198). Services for accessing these data are described at the back of the journal.

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