

Oxo-bridged haem/non-haem iron complexes

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Metallation (FeCl_2 followed by aeration) of ^5L , possessing a tris(2-pyridylmethyl)amine (tmpa) moiety tethered to a synthetic porphyrin, leads to an oxo-bridged haem/non-haem iron complex $[(^5\text{L})\text{Fe}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}(\text{Cl})]^+ \mathbf{1}$; its structure and properties compare closely with an analogue assembled *via* an acid-base synthesis, $[(\text{F}_8\text{-tpp})\text{Fe}^{\text{III}}(\text{tmpa})(\text{Cl})]^+ \mathbf{2}$ [$\text{F}_8\text{-tpp}$ = tetrakis(2,6-difluorophenyl)porphyrinate(2-)].

Interest in oxo-bridged homo- or hetero-dinuclear metal complexes derives from the versatility and bonding of the O^{2-} ligand, applications to catalysis, magnetic exchange and electron-transfer phenomena, modelling metalloprotein active sites, and synthetic considerations.¹ Here, we report the construction and preliminary characterization of members of a new class of oxo-bridged diiron complexes,² containing haem and non-haem iron mixed environments.

Ligand ^5L (Scheme 1) allows generation of dinuclear complexes where intramolecular reactions of metal ions in differing environments are favoured; it was prepared by condensation of a pyridyl 5-chloromethyl derivative of tmpa³ with a monophenol-derivatized tetraarylporphyrin. Iron insertion was accomplished by refluxing with an excess of FeCl_2 in dmf, exposure to O_2 , and precipitation of the product by the addition of brine. Counter-ion exchange using NaClO_4 followed by column chromatography affords $[(^5\text{L})\text{Fe}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}(\text{Cl})](\text{ClO}_4)$ ($\mathbf{1}\cdot\text{ClO}_4$).[†] An X-ray crystal structure analysis (Fig. 1)[‡] reveals the μ -oxo group which connects the haem and non-haem Fe^{III} atoms.⁴ The porphyrinate-iron(III) coordination closely

resembles that observed for typical high-spin μ -oxo iron(III) dimer compounds,^{5–7} while the non-haem iron(III) is six-coordinate.^{8–12} There is a pronounced bending about the oxo-bridging atom with $\text{Fe}(1)\text{--O}(1)\text{--Fe}(2) = 157.3(9)^\circ$; in contrast, porphyrinate μ -oxo iron(III) dimers⁵ and complexes of the type $[(\text{tmpa})(\text{X})\text{Fe}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}(\text{X}')(\text{tmpa})]$ ($\text{X} = \text{aquo}$, $\text{X}' = \text{ClO}_4^-$;¹³ $\text{X} = \text{X}' = \text{halide}$)⁸ exhibit near-linear $\text{Fe}\text{--O}\text{--Fe}$ angles.

$[(^5\text{L})\text{Fe}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}(\text{Cl})]^+ \mathbf{1}$ has characteristic UV-VIS absorptions at 411 (Soret) and 564 nm. A new IR absorption at 852 cm^{-1} is tentatively assigned as an $\text{Fe}\text{--O}\text{--Fe}'$ ν_{asym} stretch.⁵

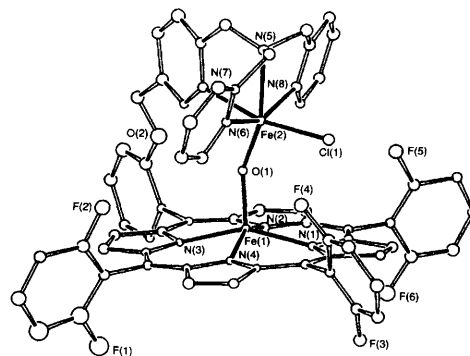
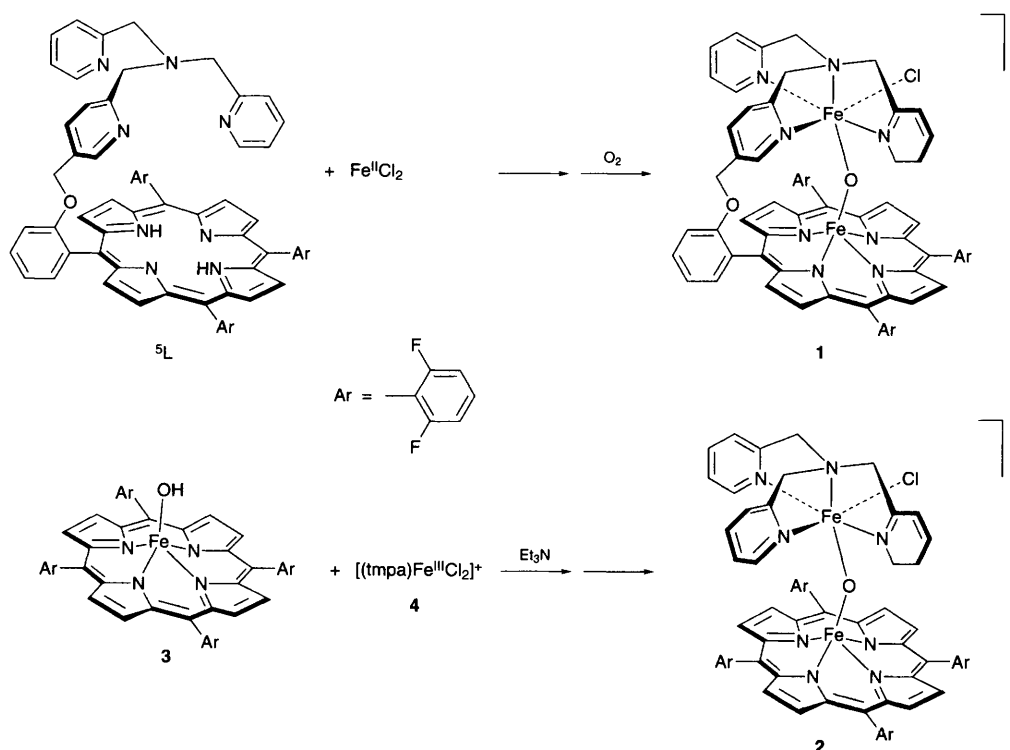


Fig. 1 ORTEP view of cation $[(^5\text{L})\text{Fe}^{\text{III}}\text{O}-\text{Fe}^{\text{III}}(\text{Cl})]^+ \mathbf{1}$. Selected bond distances (\AA): $\text{Fe}(1)\text{--O}(1)$ 1.771(14), $\text{Fe}(1)\text{--N}$ 2.079(17)–2.090(18), $\text{Fe}(2)\text{--O}(1)$ 1.783(14), $\text{Fe}(2)\text{--N}$ 2.128(18)–2.263(19), $\text{Fe}(1)\cdots\text{Fe}(2)$ 3.484(6). Selected angles ($^\circ$): $\text{Fe}(1)\text{--O}(1)\text{--Fe}(2)$ 157.3(9), $\text{Cl}(1)\text{--Fe}(2)\text{--N}(7)$ 164.9(5), $\text{O}(1)\text{--Fe}(2)\text{--N}(5)$ 165.0(7).



Scheme 1

Mössbauer spectroscopy ($\delta = 0.45 \text{ mm s}^{-1}$, $\Delta E_{\text{q}} = 1.32 \text{ mm s}^{-1}$; $\delta = 0.41 \text{ mm s}^{-1}$, $\Delta E_{\text{q}} = 0.68 \text{ mm s}^{-1}$)§ confirms the presence of two types of high-spin iron(III) atoms (1 : 1 ratio). The room-temperature magnetic moment of **1**·ClO₄ is $3.4 \mu_{\text{B}}$ indicative of antiferromagnetic coupling.^{5,8,12}

Treatment of a dichloromethane solution of **1**·ClO₄ with NaOH_(aq), followed by column chromatography affords [(⁵L)Fe^{III}-OH], containing a high-spin porphyrinate-Fe^{III}-OH moiety [UV-VIS: 413 (Soret), 571 nm] with an unmetallated tmpa moiety. 'Reconstitution' is effected by addition of iron(III) chloride to an acetone solution of [(⁵L)Fe^{III}-OH], followed by addition of Et₃N and NaClO₄, affording authentic **1**·ClO₄.

The synthesis of [(F₈-tpp)Fe^{III}-O-Fe^{III}(tmpa)(Cl)](ClO₄) (**2**·ClO₄) was accomplished via an acid-base self-assembly reaction of (F₈-tpp)Fe^{III}-OH **3**⁶ with [(tmpa)Fe^{III}Cl₂](ClO₄) **4**¹⁰ in the presence of Et₃N (Scheme 1)^{4†} An X-ray analysis (Fig. 2)‡ of **2**·ClO₄·2C₇H₁₆ confirms the proposed structure, which compares well with that of [(⁵L)Fe^{III}-O-Fe^{III}(Cl)]⁺ **1**, *vide supra*, supporting the view that the design of ⁵L ligand allows for intramolecularly formed dinuclear complexes which are essentially unstrained.

The physical and spectroscopic properties of **2** also closely resemble those observed for **1**. Optical absorptions occur at 411 (Soret) and 568 nm, while $\nu_{\text{asym}} = 852 \text{ cm}^{-1}$. Mössbauer spectroscopic properties are also very similar with $\delta = 0.45 \text{ mm s}^{-1}$, $\Delta E_{\text{q}} = 1.45 \text{ mm s}^{-1}$; $\delta = 0.40 \text{ mm s}^{-1}$, $\Delta E_{\text{q}} = 0.56 \text{ mm s}^{-1}$.§ For **2**·ClO₄ μ_{B} (room temp.) = 2.9.

In conclusion, novel haem/non-haem iron complexes with a single μ -oxo bridging ligand have been generated, either using a new dinucleating ligand, or by assembly of components in an acid-base synthesis. The ability to isolate **1** and **2** is notable, in light of the inherent stability of μ -oxo diiron(III) porphyrinates.^{5,6} Compounds **1** and **2** are structurally similar to μ -O²⁻ and μ -OH⁻ analogues [(F₈-tpp)Fe^{III}-OH-Cu^{II}(tmpa)]⁺²⁺,^{6,13} generated as models for Fe-Cu sites in haem-copper oxidases.¹⁴ Diiron species similar to **1** and **2** may also have biological

relevance. Denitrifying bacterial nitric oxide reductases are evolutionarily related to haem-copper oxidases,¹⁵ and possesses a haem centre with additional non-haem iron;¹⁶ this may comprise the catalytic core responsible for the reductive coupling of NO (giving N₂O).¹⁷

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Footnotes

† Satisfactory C, H and N elemental analyses were obtained.

‡ Crystal data: [(⁵L)Fe-O-Fe(Cl)](ClO₄), **1**·ClO₄·CH₂Cl₂·3.5C₇H₁₆·2H₂O: monoclinic, $a = 35.995(10)$, $b = 10.531(3)$, $c = 42.694(10) \text{ \AA}$, $\beta = 96.21(3)^\circ$, $V = 16097(8) \text{ \AA}^3$, space group $C2/c$, $Z = 8$, $F(000) = 7160$, $D_c = 1.42 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 5.89 \text{ cm}^{-1}$. The data were collected ($3.5 \leq 2\theta \leq 50^\circ$) at -90°C on a Rigaku AFC6S diffractometer using Mo-K α ($\lambda = 0.71069 \text{ \AA}$) radiation; 15313 reflections collected, of these 5099 [$I \geq 3\sigma(I)$] were used in the analysis; currently, $R = 0.129$, $R_w = 0.167$ (sigma weighting scheme used). [(F₈-tpp)Fe-O-Fe(tmpa)(Cl)](ClO₄)·2C₇H₁₆, **2**·ClO₄·2C₇H₁₆: orthorhombic, $a = 24.592(7)$, $b = 37.85(1)$, $c = 14.561(5) \text{ \AA}$, $V = 13555(5) \text{ \AA}^3$, space group $Pbca$, $Z = 8$, $F(000) = 5840$, $D_c = 1.39 \text{ g cm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 5.81 \text{ cm}^{-1}$. The data were collected ($3.5 \leq 2\theta \leq 50^\circ$) at -90°C using Mo-K α ($\lambda = 0.71069 \text{ \AA}$) radiation; 11943 reflections collected, of these 3217 [$I \geq 3\sigma(I)$] were used in the analysis; currently, $R = 0.11$, $R_w = 0.11$ (sigma weighting scheme used). The relatively high R factors reflect solvent disorder, which cannot be adequately modelled. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Spectra supplied to reviewers.

References

- B. O. West, *Polyhedron*, 1989, **8**, 219.
- A review on biological Fe-O-Fe is: A. L. Feig and S. J. Lippard, *Chem. Rev.*, 1994, **94**, 759, and references cited therein.
- N. Wei, D.-H. Lee, N. N. Murthy, Z. Tyeklár, K. D. Karlin, S. Kaderli, B. Jung and A. D. Zuberbühler, *Inorg. Chem.*, 1994, **33**, 4625; Z. Tyeklár, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubietta and K. D. Karlin, *J. Am. Chem. Soc.*, 1993, **115**, 2677.
- Structures with Fe^{III}-O-Fe^{III} moieties with differing ligation on each iron atom have been described: B. Maurer, J. Crane, J. Schuler, K. Wieghardt and B. Nuber, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 289.
- D. M. Kurtz Jr., *Chem. Rev.*, 1990, **90**, 585.
- K. D. Karlin, A. Nanthakumar, S. Fox, N. N. Murthy, N. Ravi, B. H. Huynh, R. D. Orosz and E. P. Day, *J. Am. Chem. Soc.*, 1994, **116**, 4753.
- W. R. Scheidt and C. A. Reed, *Chem. Rev.*, 1981, **81**, 543.
- A. Hazell, K. B. Jensen, C. J. McKenzie and H. Toftlund, *Inorg. Chem.*, 1994, **33**, 3127.
- R. A. Leising, J. Kim, M. A. Pérez and L. Que Jr., *J. Am. Chem. Soc.*, 1993, **115**, 9524.
- T. Kojima, R. A. Leising, S. Yan and L. Que Jr., *J. Am. Chem. Soc.*, 1993, **115**, 11328.
- R. E. Norman, S. Yan, L. Que Jr., G. Backes, J. Ling, J. Sanders-Loehr, J. H. Zhang and C. J. O'Connor, *J. Am. Chem. Soc.*, 1990, **112**, 1554.
- Y. Dong, H. Fujii, M. P. Hendrich, R. A. Leising, G. Pan, C. R. Randall, E. C. Wilkinson, Y. Zang, L. Que Jr., B. G. Fox, K. Kauffmann and E. Münck, *J. Am. Chem. Soc.*, 1995, **117**, 2778.
- S. Fox, A. Nanthakumar, M. Wikström, K. D. Karlin and N. J. Blackburn, *J. Am. Chem. Soc.*, 1996, **118**, 24.
- S. Iwata, C. Ostermeier, B. Ludwig and H. Michel, *Nature*, 1995, **376**, 660; T. Tsukihara, H. Aoyama, E. Yamashita, T. Tomizaki, H. Yamaguchi, K. Shinzawa-Itoh, R. Nakashima, R. Yaono and S. Yoshikawa, *Science*, 1995, **269**, 1059.
- J. van der Oost, A. P. N. de Boer, J.-W. L. de Gier, W. G. Zumft, A. H. Stouthamer and R. J. M. van Spanning, *FEMS Microbiol. Lett.*, 1994, **121**, 1; M. Saraste and J. Castresana, *FEBS Lett.*, 1994, **341**, 1.
- B. Heiss, K. Frunzke and W. G. Zumft, *J. Bacteriol.*, 1989, **171**, 3288; M. Dermastia, T. Turk and T. C. Hollocher, *J. Biol. Chem.*, 1991, **266**, 10899.
- The diiron(II) centre in reduced ribonucleotide reductase is capable of effecting this reaction: C. J. Haskin, N. Ravi, J. B. Lynch, E. Münck and L. Que Jr., *Biochemistry*, 1995, **34**, 11090.

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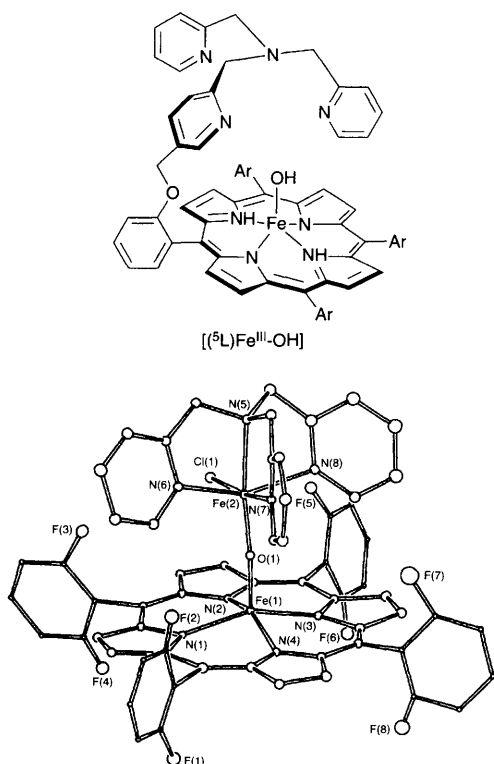


Fig. 2 ORTEP view of cation [(F₈-tpp)Fe^{III}-O-Fe^{III}(tmpa)(Cl)]⁺ **2**. Selected bond distances (Å): Fe(1)-O(1) 1.776(13), Fe(1)-N 2.069(22)-2.114(22), Fe(2)-O(1) 1.765(13), Fe(2)-N 2.159(22)-2.254(22), Fe(1)···Fe(2) 3.468(5). Selected angles (°): Fe(1)-O(1)-Fe(2) 156.8, Cl(1)-Fe(2)-N(7) 170.4(7), O(1)-Fe(2)-N(5) 165.1(7).