Oxo-bridged haem/non-haem iron complexes

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Metallation (FeCl₂ 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 [(⁵L)Feᴵᴵᴵ–O–Feᴵᴵᴵ(Cl)]⁺ 1; its structure and properties compare closely with an analogue assembled *via* an acid–base synthesis, [(F₈-tpp)Feᴵᴵᴵ(tmpa)(Cl)]⁺ 2 [F₈-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 O²⁻ 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 tmpa[3] with a monophenol-derivatized tetraarylporphyrin. Iron insertion was accomplished by refluxing with an excess of FeCl₂ in dmf, exposure to O₂, and precipitation of the product by the addition of brine. Counter-ion exchange using NaClO₄ followed by column chromatography affords [(⁵L)Feᴵᴵᴵ–O–Feᴵᴵᴵ(Cl)]-(ClO₄) (1·ClO₄).† An X-ray crystal structure analysis (Fig. 1)‡ reveals the μ-oxo group which connects the haem and non-haem Feᴵᴵᴵ 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 Fe(1)–O(1)–Fe(2) = 157.3(9)°; in contrast, porphyrinate μ-oxo iron(III) dimers[5] and complexes of the type [(tmpa)(X)Feᴵᴵᴵ–O–Feᴵᴵᴵ(X′)(tmpa)] (X = aquo, X′ = ClO₄⁻;[13] X = X′ = halide)[8] exhibit near-linear Fe–O–Fe angles.

[(⁵L)Feᴵᴵᴵ–O–Feᴵᴵᴵ(Cl)]⁺ 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 Fe–O–Fe′ $\nu_{asym.}$ stretch.[5]
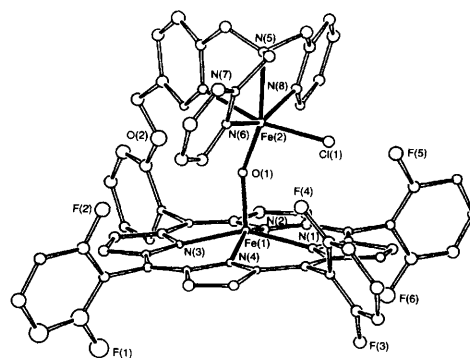
Fig. 1 ORTEP view of cation [(⁵L)Feᴵᴵᴵ–O–Feᴵᴵᴵ(Cl)]⁺ 1. Selected bond distances (Å): Fe(1)–O(1) 1.771(14), Fe(1)–N 2.079(17)–2.090(18), Fe(2)–O(1) 1.783(14), Fe(2)–N 2.128(18)–2.263(19), Fe(1)···Fe(2) 3.484(6). Selected angles (°): Fe(1)–O(1)–Fe(2) 157.3(9), Cl(1)–Fe(2)–N(7) 164.9(5), O(1)–Fe(2)–N(5) 165.0(7).
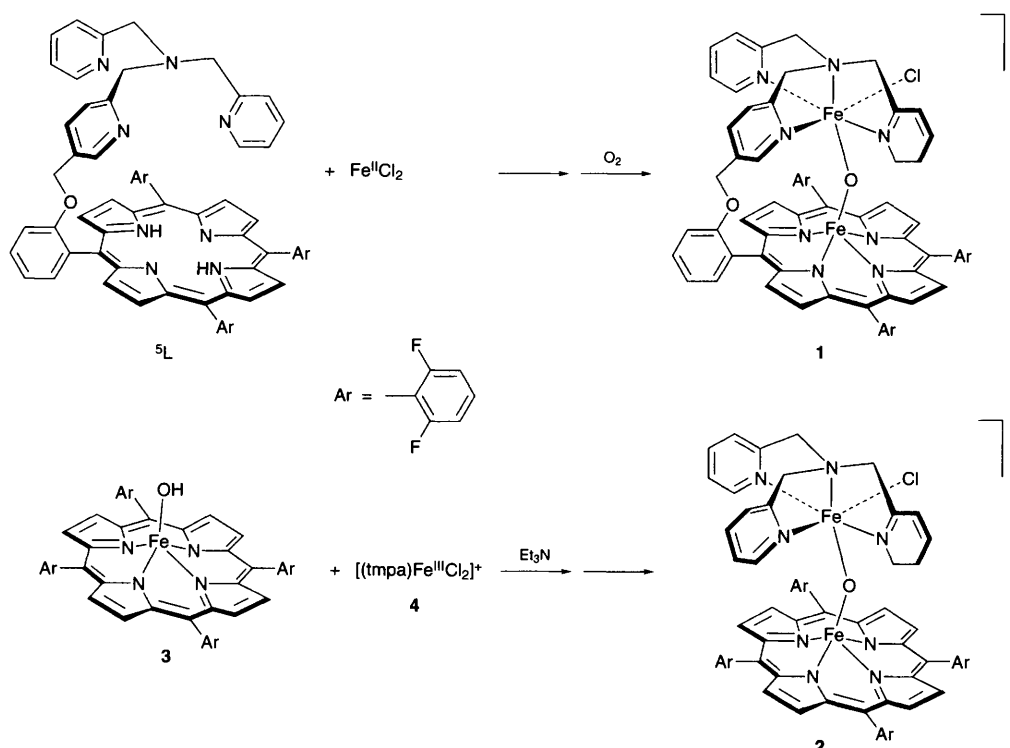
Scheme 1

Mössbauer spectroscopy (δ = 0.45 mm s^{-1}, ΔE_q = 1.32 mm s^{-1}; δ = 0.41 mm s^{-1}, ΔE_q = 0.68 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·ClO$_4$ is 3.4 μ_B indicative of antiferromagnetic coupling.[5,8,12]

Treatment of a dichloromethane solution of 1·ClO$_4$ with NaOH$_{(aq)}$, followed by column chromatography affords [(^{5}L)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 [(^{5}L)Fe^{III}–OH], followed by addition of Et$_3$N and NaClO$_4$, affording authentic 1·ClO$_4$.

The synthesis of ([F$_8$-tpp)Fe^{III}–O–Fe^{III}(tmpa)(Cl)](ClO$_4$) (2·ClO$_4$) was accomplished via an acid–base self-assembly reaction of (F$_8$-tpp)Fe^{III}–OH 3[6] with [(tmpa)Fe^{III}Cl$_2$](ClO$_4$) 4[10] in the presence of Et$_3$N (Scheme 1)[4]† An X-ray analysis (Fig. 2)‡ of 2·ClO$_4$·2C$_7$H$_{16}$ confirms the proposed structure, which compares well with that of [(^{5}L)Fe^{III}–O–Fe^{III}(Cl)]$^+$ 1, vide supra, supporting the view that the design of ^{5}L 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 ν_{asym} = 852 cm^{-1}. Mössbauer spectroscopic properties are also very similar with δ = 0.45 mm s^{-1}, ΔE_q = 1.45 mm s^{-1}; δ = 0.40 mm s^{-1}, ΔE_q = 0.56 mm s^{-1}.§ For 2·ClO$_4$ 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-O^{2-} and µ-OH$^-$ analogues [(F$_8$-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 N$_2$O).[17]

Footnotes

† Satisfactory C, H and N elemental analyses were obtained.
‡ Crystal data: [(^{5}L)Fe–O–Fe(Cl)](ClO$_4$), 1·ClO$_4$·CH$_2$Cl$_2$·3.5C$_7$H$_{16}$·2H$_2$O: monoclinic, a = 35.995(10), b = 10.531(3), c = 42.694(10) Å, β = 96.21(3)°, V = 16097(8) Å^3, space group C2/c, Z = 8, F(000) = 7160, D$_c$ = 1.42 g cm^{-3}, µ(Mo-Kα) = 5.89 cm^{-1}. The data were collected (3.5 ≤ 2θ ≤ 50°) at −90 °C on a Rigaku AFC6S diffractometer using Mo-Kα (λ = 0.71069 Å) radiation; 15313 reflections collected, of these 5099 [I ≥ 3σ(I)] were used in the analysis; currently, R = 0.129, R$_w$ = 0.167 (sigma weighting scheme used). [(F$_8$-tpp)Fe–O–Fe(tmpa)(Cl)](ClO$_4$)·2C$_7$H$_{16}$, 2·(ClO$_4$)·2C$_7$H$_{16}$; orthorhombic, a = 24.592(7), b = 37.85(1), c = 14.561(5) Å, V = 13555(5) Å^3, space group Pbca, Z = 8, F(000) = 5840, D$_c$ = 1.39 g cm^{-3}, µ(Mo-Kα) = 5.81 cm^{-1}. The data were collected (3.5 ≤ 2θ ≤ 50°) at −90 °C using Mo-Kα (λ = 0.71069 Å) radiation; 11943 reflections collected, of these 3217 [I ≥ 3σ(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

1 B. O. West, Polyhedron, 1989, 8, 219.
2 A review on biological Fe–O–Fe is: A. L. Feig and S. J. Lippard, Chem. Rev., 1994, 94, 759, and references cited therein.
3 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. Zubieta and K. D. Karlin, J. Am. Chem. Soc., 1993, 115, 2677.
4 Structures with Fe^{III}–O–Fe^{III} moieties with differing ligation on each iron atom have been described: B. Mauerer, J. Crane, J. Schuler, K. Wieghardt and B. Nuber, Angew. Chem., Int. Ed. Engl., 1993, 32, 289.
5 D. M. Kurtz Jr., Chem. Rev., 1990, 90, 585.
6 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.
7 W. R. Scheidt and C. A. Reed, Chem. Rev., 1981, 81, 543.
8 A. Hazell, K. B. Jensen, C. J. McKenzie and H. Toftlund, Inorg. Chem., 1994, 33, 3127.
9 R. A. Leising, J. Kim, M. A. Pérez and L. Que Jr., J. Am. Chem. Soc., 1993, 115, 9524.
10 T. Kojima, R. A. Leising, S. Yan and L. Que Jr., J. Am. Chem. Soc., 1993, 115, 11328.
11 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.
12 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.
13 S. Fox, A. Nanthakumar, M. Wikström, K. D. Karlin and N. J. Blackburn, J. Am. Chem. Soc., 1996, 118, 24.
14 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.
15 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.
16 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.
17 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.

[(^{5}L)Fe^{III}-OH]
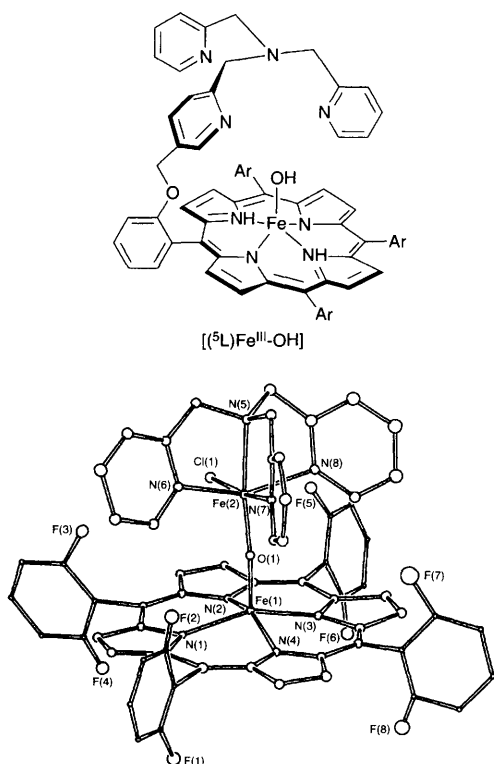
Fig. 2 ORTEP view of cation [(F$_8$-tpp)Fe^{III}–O–Fe^{III}(tmpa)(Cl)]$^+$ 2. Selected bond distances (Å): Fe(1)–O(1) 1.776(13), Fe(1)–N 2.069(22)–2.114(22), Fe(2)–O(1) 1.765(13), Fe(2)–N 2.159(22)–2.254(22), Fe(1)···Fe(2) 3.468(5). Selected angles (°): Fe(1)–O(1)–Fe(2) 156.8, Cl(1)–Fe(2)–N(7) 170.4(7), O(1)– Fe(2)–N(5) 165.1(7).