meso-Octamethyl-porphyrinogen Metal Complexes: an Entry to High Valent Unsaturated Metal Centres

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The *meso*-octamethyl porphyrinogen tetraanion has been used to bind iron(III) and oxomolybdenum(V) ions; X-ray analysis revealed the interaction of a square-planar tetracoordinate Fe^{III} and the oxo group in the Mo^{V} complex with the *meso*-methyls.

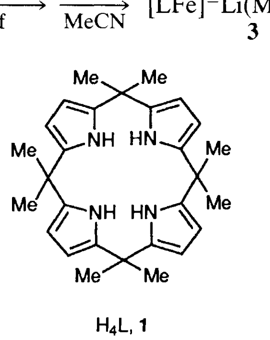
The *meso*-octamethyl porphyrinogen, **1**,[1,2] which has never been used to our knowledge for metal complexation, should function as a tetraanionic N_4 ligand suitable for stabilizing high oxidation states for transition metals. In addition, on close examination of the conformations[3] of such a ligand with *meso*-substituents, we became aware of the potential role of the *meso*-alkyl groups in protection and/or interaction with the metal centre.

The synthesis of **1** was performed as reported several years ago;[1b,g] it was reacted with $LiBu^n$ in tetrahydrofuran (thf) to form the corresponding crystalline lithium salt, **2**, (84%), eqn. (1).

$$\underset{\mathbf{1}}{H_4L} \xrightarrow[-Bu^nH]{thf,\ LiBu^n} \underset{\mathbf{2}}{[LLi_4(thf)_4]} \qquad (1)$$

Upon reacting $FeCl_2(thf)_{1.5}$ with **2** in a 2 : 1 molar ratio in thf, a deep-red solution was obtained. Evaporation of the solvent gave a residue, which was crystallised from toluene–acetonitrile (90%) as **3**,† eqn. (2).

$$\underset{\mathbf{2}}{[LLi_4(thf)_4]} \xrightarrow[thf]{FeCl_2\cdot thf_{1.5}} \xrightarrow[MeCN]{toluene} \underset{\mathbf{3}}{[LFe]^{-}Li(MeCN)_4^{+}} \qquad (2)$$



H_4L, **1**

The formation of an iron(III) derivative does not arise from air oxidation, but is much more likely from an iron(II) disproportionation reaction; such a mechanism is now under investigation. Complex **3** is extremely sensitive to oxidants. A top view and a side view of the structure of the anion in **3** are shown in Fig. 1*a* and 1*b*.‡ Iron(III) has a strictly planar coordination geometry provided by the four deprotonated nitrogens of the ligand **1**. The six-membered chelation rings have a boat conformation and they alternatively tilt up and

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† Satisfactory analytical data have been obtained for **2**, **3** and **4**.

‡ *Crystal data* for **3**: $C_{28}H_{32}FeN_4\cdot C_8H_{12}LiN_4$, $M = 651.6$, monoclinic, space group $P2_1/m$, $a = 9.277(1)$, $b = 15.590(2)$, $c = 13.009(1)$ Å, $\beta = 93.14(1)°$, $U = 1878.7(3)$ Å^3, $Z = 2$, $D_c = 1.152$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 4.32 cm^{-1}, crystal dimensions 0.95 × 0.93 × 0.40 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and anisotropically refined by full-matrix least-squares. For 2695 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Siemens AED diffractometer in the range $6° < 2\theta < 52°$, the R value is 0.044 (R_w = 0.046). The hydrogen atoms were located from difference maps and introduced as fixed contributors in the final stage of refinement. All calculations were carried out using SHELX76. **4**, $C_{28}H_{32}MoN_4O\cdot C_{16}H_{32}LiO_4$, $M = 831.9$, monoclinic, space group $P2_1/n$, $a = 11.469(2)$, $b = 27.666(4)$, $c = 13.817(3)$ Å, $\beta = 93.42(1)°$, $U = 4376.4(6)$ Å^3, $Z = 4$, $D_c = 1.263$ g cm^{-3}, Mo-Kα radiation ($\lambda = 0.71069$ Å), μ(Mo-Kα) = 3.34 cm^{-1}, crystal dimensions 1.10 × 0.40 × 0.25 mm. The structure was solved by the heavy atom method (Patterson and Fourier synthesis) and anisotropically refined (except for the thf molecules and Li atom) by full-matrix least-squares. For 2248 unique observed structure amplitudes $[I > 2\sigma(I)]$ collected at room temperature on a Philips PW1100 diffractometer in the range $6° < 2\theta < 46°$, the R value is 0.077 (R_w = 0.082). The hydrogen atoms were placed in idealized positions and introduced as fixed contributors in the final stage of refinement; thf molecules were refined as rigid bodies. All calculations were carried out using SHELX76. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

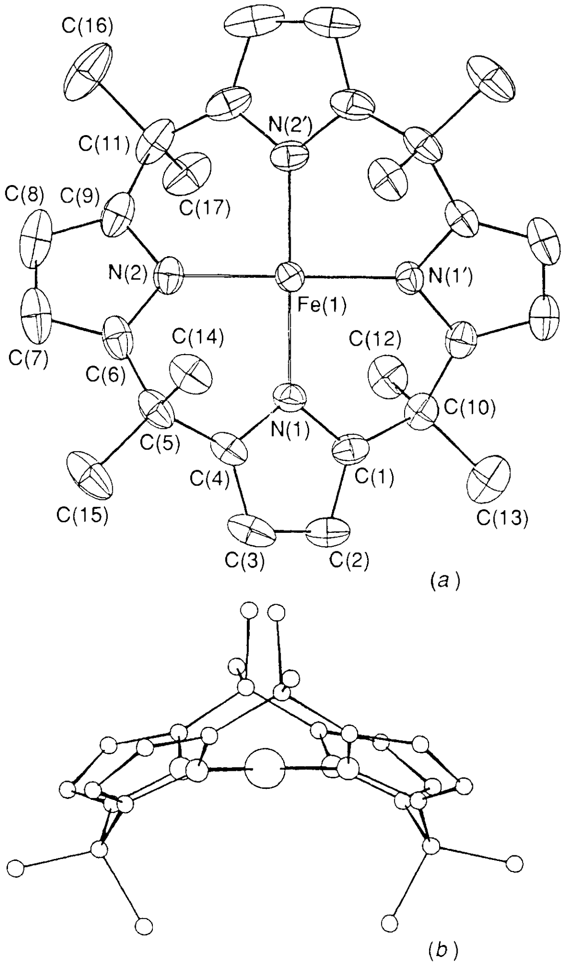


Fig. 1 (*a*) An ORTEP view of the anion in complex **3** (30% probability ellipsoids). Bond distances (Å): Fe(1)–N(1), 1.888(2); Fe(1)–N(2), 1.882(2). Bond angles (°): N(1)–Fe(1)–N(2′), 179.9(1); N(1)–Fe(1)–N(1′), 89.7(1); N(1)–Fe(1)–N(2), 90.4(1). Prime denotes a transformation of *x*, 1/2 − *y*,*z*. (*b*) Side view of the anion in complex **3**.

down determining a double saddle shape conformation for the tetraanion. The dihedral angle between the planar pyrroles is 45.8(1)°, while they form dihedral angles of 32.8(1) and 31.5(1)° with the coordination plane FeN_4. The axial coordination positions of the iron are filled by *meso* methyl groups, the C · · · C separation being 4.45 Å for C(12) · · · C(17) and 4.32 Å for C(14) · · · C(14′). Four hydrogen atoms from C(12), C(14), C(14′) and C(17) provide a flattened tetrahedral cage for the iron bisected by the coordination plane, the iron–hydrogen distances being Fe · · · H(12,1), 2.84, Fe · · · H(14,1), 2.83 and Fe · · · H(17,1) 2.91 Å. Such iron–hydrogen interactions, if really effective, should modify the properties expected for a purely square-planar iron(III) ion. The magnetic moment of 4.35 μ_B at 293 K is hardly understandable for iron(III) in a square-planar coordination, unless we consider the *meso*-methyl hydrogens acting like axial ligands. Temperature dependent magnetic susceptibility measurements will give more insight on such a question.

The reaction of **2** with $MoOCl_4$ in thf of other solvents, followed by treatment in thf gave a green solution; after evaporation to dryness, deep-green crystals of **4**[†] (60%) were recrystallised from THF–toluene, eqn. (3).

$$\underset{\mathbf{2}}{[LLi_4(thf)_4]} \xrightarrow[\text{thf–toluene}]{MoOCl_4} \underset{\mathbf{4}}{[LMo(O)]^-[Li(thf)_4]^+} \qquad (3)$$

Complex **4** is an Mo^V derivative with a magnetic moment of 1.70 μ_B at 293 K. Reduction of Mo^{VI} to Mo^V in solvents like thf is quite a common phenomenon. The introduction of a functional group greatly affects the conformation of ligand **1**.[3] Fig. 2 shows the top (*a*) and side (*b*) views of the anion **4**.[‡] The structure of **4** has been solved assuming a symmetric statistical distribution (84%, A) above and (16%, B) below the N_4 plane by 0.619(1) Å for the molybdenum atom. The conformation of the macrocycle ligand is significantly different from that in **3**, as exemplified by the dihedral angles between the planar pyrroles ranging from 26.3(6) to 51.6(7)°, and the dihedral angles of the pyrroles with the N_4 plane ranging from 24.0(5) to 26.9(5)°. The distortion of the ligand caused by the oxo functionality at the metal is emphasized by the difference in the C · · · C separation for the *meso*-methyl groups, being 4.76(3) Å for C(23) · · · C(27) and 6.23(3) Å for C(22) · · · C(26). The role of the *meso*-methyl groups remains an essential characteristic of the present ligand. Significant close contacts have been observed between the C(22) and C(26) methyls and the oxo functionality [C(22) · · · O(1A), 3.152(21) Å; C(22) · · · H(22,1), 1.06 Å; H(22,1) · · · O(1A), 2.111 Å; C(22) · · · H(22,1) · · · O(1A), 161°; C(26) · · · O(1A), 3.100(22) Å; C(26)–H26,1; 1.06 Å; H(26,1) · · · O(1A), 2.102 Å; C(26) · · · H(26,1) · · · O(1A), 156°]. Such close contacts mimic a sort of transition state (X) in the mechanism of oxotransfer to unactivated C–H bonds.

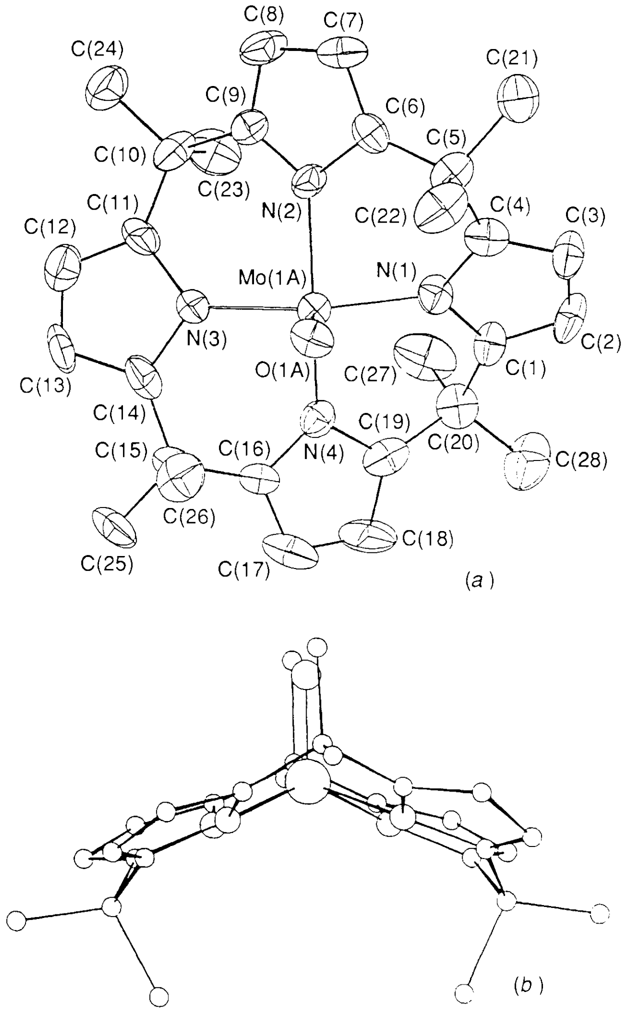
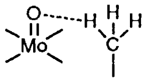


Fig. 2 (*a*) An ORTEP view of the anion in complex **4** (30% probability ellipsoids). Bond distances (Å): Mo(1A)–O(1A), 1.655(10); Mo(1A)–N(1), 2.038(11); Mo(1A)–N(2), 2.045(12); Mo(1A)–N(3), 2.070(11); Mo(1A)–N(4), 2.079(11). Bond angles (°): N(3)–Mo(1A)–N(4), 82.7(4); N(2)–Mo(1A)–N(4), 145.7(4); N(2)–Mo(1A)–N(3), 85.8(5); N(1)–Mo(1A)–N(4), 86.5(4); N(1)–Mo(1A)–N(3), 144.2(4); N(1)–Mo(1A)–N(2), 84.2(5). (*b*) Side view of the anion in complex **4**.



(X)

Ligand **1** allows a close contact between metals or inorganic functionalities and unactivated C–H groups, and generation of unsaturated high oxidation states at the metal. Its use with a varity of metal ions is under investigation.

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