# X-Ray Crystal Structure of a Planar, High-spin Iron(II) Complex of a Pentadentate Unsaturated Macrocycle formed by Reaction of 2,9-Di(1-methylhydrazino)1,10-phenanthroline Monohydrochloride with 2,6-Diacetylpyridine

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Summary The crystal structure of a high spin iron(II) complex with a pentadentate nitrogen macrocycle, that bears certain structural similarities to porphyrins, demonstrates that the metal ion sits in the ligand plane, a stereochemistry that is attributed to the slightly larger hole size relative to porphyrins.

INTEREST in the correlation between the spin state of Fe^{II} in porphyrin complexes and the position of this metal ion relative to the ligand plane has been sustained by the possible relevance to the mechanism of oxygen transport by haemoglobin.[1,2] Low spin $(S=0)$[3] and intermediate spin $(S=1)$[4] Fe^{II} ions can occupy porphyrin cavities, but it is predicted[2] and calculated[5] that high spin Fe^{II} will be displaced from the plane, owing to the increase in the radius of the metal ion. In a previous communication[6] we reported the structure of $[Mn(L)Cl][BF_4]$, where L is the rigid ligand (1). The ligand L has a 'hole' size similar to

L

(1)

† 1 B.M. $= 9\cdot27 \times 10^{-24}$ A m².
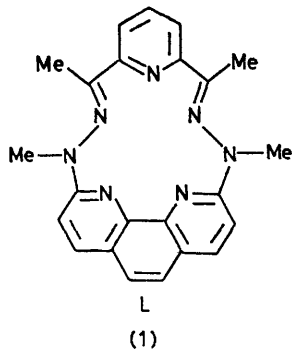
that of porphyrins, and we now describe the stereochemistry of an Fe^{II} complex of this ligand; the high spin metal ion sits at the centre of the macrocyclic cavity.

The complex $[Fe(L)(H_2O)_2][BF_4]_2$ was prepared by the condensation of 2,9-di-(1-methylhydrazino)-1,10-phenanthroline monohydrochloride with 2,6-diacetylpyridine in deoxygenated refluxing water, with an iron(II) salt acting as a template. Addition of $NaBF_4$, followed by cooling, gave olive green platelets. The magnetic susceptibility (X_M) of this complex was measured over the temperature range 93—293 K by the Gouy method. A plot of $1/X_M$ against temperature is a straight line, the gradient of which gives $\mu_{eff} = 5\cdot33$ B.M.† while the intercept of -32 K is the Weiss constant. The room temperature Mössbauer parameters of this complex, an isomer shift of $1\cdot01$ mm s⁻¹ relative to natural iron and a quadrupole splitting of $2\cdot74$ mm s⁻¹, are consistent with high spin Fe^{II}.[7]

Crystal data: $C_{23}H_{25}B_2F_8FeN_7O_2$, $M = 660\cdot97$, monoclinic, $a = 14\cdot152(3)$, $b = 11\cdot464(11)$, $c = 16\cdot732(5)$ Å, $\beta = 93\cdot56-(3)°$, $U = 2709\cdot3$ Å³; $D_c = 1\cdot620$ g cm⁻³, $Z = 4$, $\mu(Mo-K_\alpha) = 608$ cm⁻¹; space group $P2_1/c$. 5319 intensities (layers 0—$h,13,l$) were recorded on a Stoe STADI-2 two-circle diffractometer, using graphite-monochromated Mo-K_α radiation. A numerical absorption correction was applied, and equivalent reflections averaged to give 3106 unique observed intensities $[I > 3\sigma(I)]$ which were used in structure solution. The fractional atomic co-ordinates of the Fe atom were derived from a Patterson synthesis, and the lighter atoms from subsequent Fourier difference maps. The structure was refined using blocked full-matrix least-squares (Fe, N, and O atoms anisotropic, C and B individual isotropic, methyl H, aromatic H, and F common isotropic temperature factors). The C–H distances were fixed at 1·08 Å with the aromatic hydrogens lying on the C–C–C

angle bisector, and the methyl hydrogens defining three vertices of a tetrahedron. Both $[BF_4]^-$ groups were severely disordered, and all but two of the fluorines were refined as partial atoms in two sites, with occupancy factors k and $1 - k$, respectively. The current R is 0·108, and $R_w[=\Sigma_w{}^{\frac{1}{2}}\Delta/\Sigma_w{}^{\frac{1}{2}}|F_0|] = 0\cdot105$.
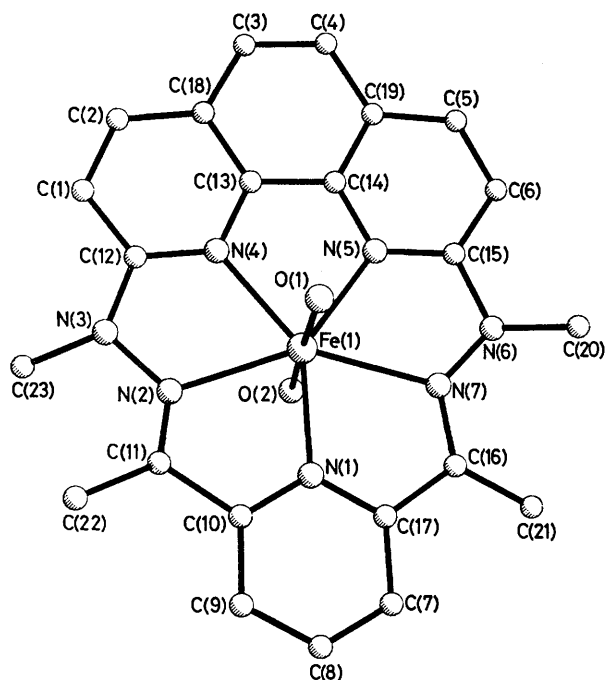

FIGURE. The molecular structure of $[Fe(L)(H_2O)_2]^{2+}$, hydrogen atoms have been omitted for clarity. Bond lengths: Fe(1)–O(1), 2·213(7); Fe(1)–O(2), 2·194(7); Fe(1)–N(1), 2·100(9); Fe(1)–N(2), 2·242(8); Fe(1)–N(4), 2·126(7); Fe(1)–N(5), 2·112(8); Fe(1)–N(7), 2·276(8); N(2)–N(3), 1·39(1); and N(6)–N(7), 1·36(1) Å; and angles, O(1)–Fe(1)–O(2), 177·6(3); N(1)–Fe(1)–N(2), 72·8(3); N(2)–Fe(1)–N(4), 70·1(3); N(4)–Fe(1)–N(5), 75·0(3); N(5)–Fe(1)–N(7), 69·8(3); and N(7)–Fe(1)–N(1), 72·3(3)°.

The molecular geometry of the cation is shown in the Figure, which includes some important bond lengths and angles. The Fe^{II} is seven-co-ordinate with the donor atoms at the vertices of a slightly distorted pentagonal bipyramid. Two water molecules occupy the axial sites with an average Fe–O distance of 2·204 Å, and the two anions are unco-ordinated. The iron atom is co-planar with the nitrogens (maximum deviation from the FeN_5 plane is 0·018 Å). Angles subtended by adjacent nitrogen donors at the metal ion lie in the range 69—75°, while two metal–nitrogen [Fe(1)–N(2) and Fe(1)–N(7)] distances are significantly longer than the other three. The ligand is approximately planar with the major deviations from planarity being caused by the short intramolecular contacts between pairs of adjacent methyl groups.‡

The crystal structure of $[Mn(L)Cl][BF_4]$ demonstrated[6] certain similarities between porphyrins and L(1), in that both types of compound are planar, relatively rigid, and appear to have π-electron delocalisation present. The 'hole' size in L is slightly greater than is found in $\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin (TPP) but the distance of the Mn^{II} atom from the plane of L, 0·53 Å, is close to the displacement of 0·51 Å reported for (1-MeIm)Mn(TPP) (1-MeIm = 1-methylimidazole).[8] However, the difference in cavity sizes is crucial to the co-ordination geometry of the corresponding high spin iron(II) complexes, where the metal ion is slightly smaller.[9] The Fe–N distance of 2·086 Å found in the high spin complex, (2-MeIm)Fe(TPP), still results in the Fe^{II} sitting out of the plane,[4] but this distance is less than the shortest Fe–N bond length, 2·10 Å, in $[Fe(L)(H_2O)_2]$ $[BF_4]_2$. Thus, while for Fe^{II} to be co-planar with porphyrins spin pairing has to occur, as in diamagnetic $(pip)_2Fe(TPP)$ (pip = piperidine) where[3] Fe–N is 2·004(4) Å, and intermediate spin Fe(TPP) with Fe–N = 1·972(4) Å,[4] the high spin Fe^{II} ion can sit at the centre of L. This result illustrates the influence of macrocyclic 'hole' size on the co-ordination geometry of the Fe^{II} ion, and provides indirect support for the proposed mechanism of the co-operative effect in haemoglobin.[1] A related 7-co-ordinate system in which the ligand is not as rigid as (1) shows distortion from planarity of the Fe–N_5 system.[10]

‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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