Molecular Stereochemistry and Crystal Structure of a 'Spin-equilibrium' ($S = 1/2$, $S = 5/2$) Haemichrome Salt: Bis-(3-chloropyridine)octaethylporphinatoiron(III) Perchlorate

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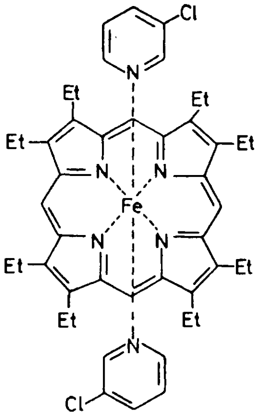
Summary The molecular stereochemistry of a haemichrome salt, bis-(3-chloropyridine)octaethylporphinatoiron(III) perchlorate, has been determined; the structural parameters of the co-ordination group are in accord with a spin-equilibrium between two states, $S = 1/2$ and $S = 5/2$.

The temperature dependence of the effective magnetic moment of a number of haemichrome salts has been recently reported.[1] These temperature dependent moments were interpreted in terms of an equilibrium between two spin states with $S = 1/2$ and $S = 5/2$. We now report the preparation of a single crystal of one such derivative, bis-(3-chloropyridine)octaethylporphinatoiron(III) perchlorate, $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+\ \text{ClO}_4^-$ (**1**) and the determination of its X-ray crystal structure at 293 K. The molecular structure of $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+$ is in good agreement with the suggested equilibrium;[1] however, the axial Fe–N(py) bond distances appear to be surprisingly insensitive to the change in spin state.



(1)

Crystal data: $\text{Fe(N}_4\text{C}_{36}\text{H}_{44})\ (\text{ClNC}_5\text{H}_4)_2\text{ClO}_4$, $M = 915{\cdot}2$, triclinic, $a = 10{\cdot}929(3)$, $b = 11{\cdot}480(2)$, $c = 9{\cdot}954(2)$ Å, $\alpha = 112{\cdot}27(1)$, $\beta = 94{\cdot}30(2)$, $\gamma = 73{\cdot}34(2)°$, $U = 1106{\cdot}45$ Å^3, $D_\text{c} = 1{\cdot}37$, $D_\text{m} = 1{\cdot}39$ g cm^{-1}, $Z = 1$; space group $P1$ or $P\bar{1}$; Mo-K_α radiation (graphite monochromator), $\lambda = 0{\cdot}71073$ Å.

Intensity data were measured to $2\theta < 59°$ by θ—2θ scanning and a total of 5228 reflections with $F_\text{o} > 3\sigma(F_\text{o})$ were used in the refinement. A Patterson map was consistent with the space group $P\bar{1}$. The crystal lattice is composed of discrete $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+$ cations and ClO_4^- anions with the Fe atom lying on an inversion centre and the ClO_4^- ion disordered around a second inversion centre. Since the ClO_4^- tetrahedron cannot be accommodated on an inversion centre, statistical disorder for the ClO_4^- ion had to be assumed and each atom was assigned an occupancy of 0·5.† The structure was refined by a combination of full-matrix and block-diagonal least squares to a current $R = \Sigma|\ |F_\text{o}| - |F_\text{c}|\ |/\Sigma|F_\text{o}| = 0{\cdot}051$ and $R = [\Sigma_w(|F_\text{o}| - |F_\text{c}|)^2/\Sigma_w(F_\text{o})^2]^{1/2} = 0{\cdot}069$. The refinement was exceptionally well behaved and it was possible to refine even the co-ordinates and temperature factors of the hydrogen atoms (final data/parameter ratio is 13·1).

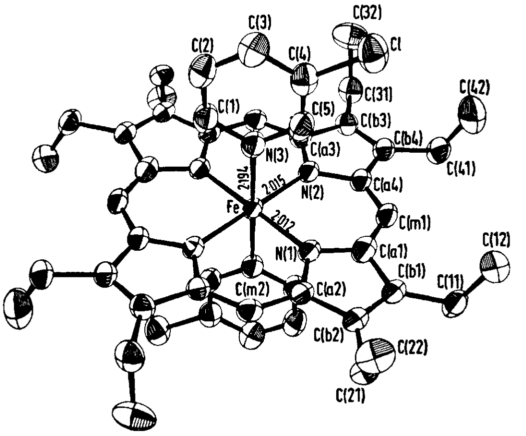


Figure. A perspective view of the $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+$ ion. Hydrogen atoms have been omitted. Pertinent bond distances are shown and have standard deviations of 0·002 Å.

The structure of the $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+$ ion and bond parameters for the iron co-ordination group are shown in the Figure. The clearly six-co-ordinate iron(III) ion is rigorously centred in the porphinato plane. The Fe–N (porphyrin) distances of 2·012(2) and 2·015(2) Å are about halfway between the 1·989 Å value observed for several low-spin porphinatoiron(III) derivatives[2–4] and the 2·045 Å value observed for two high-spin six-co-ordinate iron(III) derivatives.[5,6] Assuming that the Fe–N distances in $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+$ are linearly proportional to the fraction of the high- and low-spin states, the structure thus suggests approximately equal populations of the two states, in excellent agreement with the measured susceptibility ($\mu = 4{\cdot}8$ B.M.) of our crystalline sample. An e.s.r. examination of solid $[\text{Fe(oep)}\ (3\text{-Clpy})_2]^+$ (at room temperature and 95 K) did not show features expected for either high-spin or low-spin iron(III) haems. The lack of an e.s.r.

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† 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.

signal is attributed to either spin–lattice relaxation effects or a rapid low-spin/high-spin thermal equilibrium.

The axial Fe–N(py) bond distance of 2·194(2) Å is substantially longer than the 1·96—1·99 Å values observed for bis(imidazole) complexes[2,3] or the 2·089 Å value observed for Fe–N(py) in low-spin Fe(tpp)(py)(N_3) (tpp = tetraphenylporphinato).[4] The thermal parameters of the pyridine ligand atoms are not significantly larger than those of the atoms in the porphinato core. This suggests that positional disorder of the pyridine ligand is not much larger than the ±0·025—0·030 Å displacements possible in the porphinato core. Thus the differences in the Fe–N(py) bond distances for the two spin states of $[\mathrm{Fe(oep)\,(3\text{-}Clpy)_2}]^+$ appear to be conservatively estimated to be less than 0·10 Å. An accurate determination of this bond distance in the low-spin form of the complex must await our determination of structure at low temperature.

The present results strongly suggest that the structural changes accompanying the spin state change ($S = 1/2 \rightarrow 5/2$) are porphinato core expansion[5,6] and some elongation of the axial bonds. Similar phenomena may be occurring in two recently reported six-co-ordinate iron(III) haems[7,8] which have Fe–N bond distances shorter than the 2·045 Å value appropriate for high-spin complexes.

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