Crystal Structure of Monomeric Hydrated Iron(III) 5,10,15,20-Tetra(*N*-methyl-4-pyridinio)porphyrin Pentachloride; an Ionic Haem Model†

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The crystal structure of hydrated iron(III) 5,10,15,20-tetra(*N*-methyl-4-pyridinio)porphyrin pentachloride has been determined. It crystallises as high-spin six-co-ordinated diaqua monomers (molecular symmetry $\bar{1}$). The iron atom lies in the plane of a flat porphyrin ring [Fe–N(porphyrin), 2.042(6) and 2.038(7) Å]. The axial water ligands [Fe–H_2O 2.086(5) Å] are hydrogen-bonded to chloride ions and water molecules in a network of negative charges that interlace between the positively charged iron(III) porphyrins.

The reactions of iron(III) and manganese(III) tetraarylporphyrins with monooxygen donors have been extensively employed to model the chemistry of haem enzymes and to develop new oxidation catalysts.[1] An important part of this work has involved studies with charged tetraaryl metalloporphyrins in homogeneous solution[2] or supported on polar surfaces.[3] Despite the interest in these polar catalysts there are no reports of the crystal structures of their monomeric iron(III) or manganese(III) derivatives. Scheidt and his co-workers have published a preliminary X-ray crystallographic study of the bis(imidazole) complex of nickel(II) 5,10,15,20-tetra(*N*-methyl-4-pyridinio)porphyrin[4] Ni^{II}(tmpyp) and very recently they reported the structure of the octaperchlorate of the μ-oxo dimer of Fe^{III}(tmpyp).[5] In the latter study the iron atoms were shown to be five-co-ordinated and displaced out of the porphyrin plane by 0.47 Å. Attempts by Scheidt's group to obtain crystal structures of a monomeric hydrated pentaperchlorate of Fe^{III}(tmpp) were abandoned owing to difficulties with solvent and counter ion disorder.

In this paper we report the first crystal structure of a monomeric charged iron(III) tetraarylporphyrin, [Fe^{III}(tmpyp)]Cl_5·$n$$H_2O$.

Experimental

High-spin [Fe^{III}(tmpyp)]$^{5+}$ was prepared as reported previously[3e] and recrystallised as microcrystals by the liquid-diffusion method using acetone–water (10:1). All attempts to prepare larger crystals were unsuccessful. Crystals with two different morphologies, thin needles and plates, were obtained. Only the latter were suitable for structural investigations. One crystal (approximate volume 10^{-4} mm^3) was used to elucidate the crystal structure.

The iron porphyrin had λ_{max}(water, pH 7.02) 338, 424 (ε = 10 000 m^2 mol^{-1}), 506, 596 and 635 nm; δ_H(CD_3OD) 80.5 (br s, 8 H), 13.15 (s, 8 H), 11.9 (s, 8 H) and 6.75 (s, 12 H) (Found: C, 50.9; H, 4.50; Fe, 5.6; N, 10.55. $C_{44}H_{36}Cl_5FeN_8$·$7H_2O$ requires C, 51.00; H, 4.85; Fe, 5.40; N, 10.80%). The number of water molecules associated with each iron porphyrin has been found to vary from batch to batch depending on the dryness of the material, and presumably on the crystal form. The magnetic susceptibility (μ_{eff}) of the microcrystals was measured with a Newport Instruments Gouy balance, calibrated with copper(II) sulphate pentahydrate, and was found to be 5.66 μ_B.

Crystal Structure Determination.—Crystal data. $C_{44}H_{36}Cl_5$-FeN_8·$9H_2O$, M = 1072.1, monoclinic, space group $P2_1/c$, a = 13.53(2), b = 11.67(2), c = 16.17(2) Å, U = 2430(6) Å^3, β = 107.85(5)° (determined from 241 reflections over two mutually perpendicular regions of reciprocal space: resolution range 6–0.8 Å), Z = 2, D_c = 1.47(1) g cm^{-3}, F(000) = 1114. Purple-red, triangular flat plate, approximate volume 10^{-4} mm^3.

Data collection and processing. All attempts to collect the data by conventional means were unsuccessful. The data reported here were collected on the FAST detector at the Synchrotron Radiation Source, SERC Daresbury Laboratory, Warrington, with a wavelength of 0.865(2) Å to a d spacing of less than 1 Å. Raw data were processed with the program MADNES[6] using box integration, which automatically flags for rejection a high percentage of weak reflections at high Bragg angle. Subsequent scaling and merging yielded 1822 reflections to 1 Å, and 176 reflections at higher resolution. This corresponds to 64% of the theoretically observable data to a resolution of 1 Å. The merging R_I was 0.049 with an average multiplicity of 2.2.

Structure analysis and refinement. The structure was solved using Patterson and Fourier difference techniques and refined by blocked full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms. For each iron porphyrin, five chloride ions (one of which is disordered) and nine water molecules [one sharing the Cl(3) position] were identified from the difference maps. At the later stages of refinement porphyrin hydrogens were included in the structure-factor calculations at their computed positions. The final R_F for 1981 reflections was 0.068. Map calculations and refinement were performed with the program SHELX 76.[7]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

The data show that [Fe^{III}(tmpyp)]$^{5+}$ crystallises as discrete

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

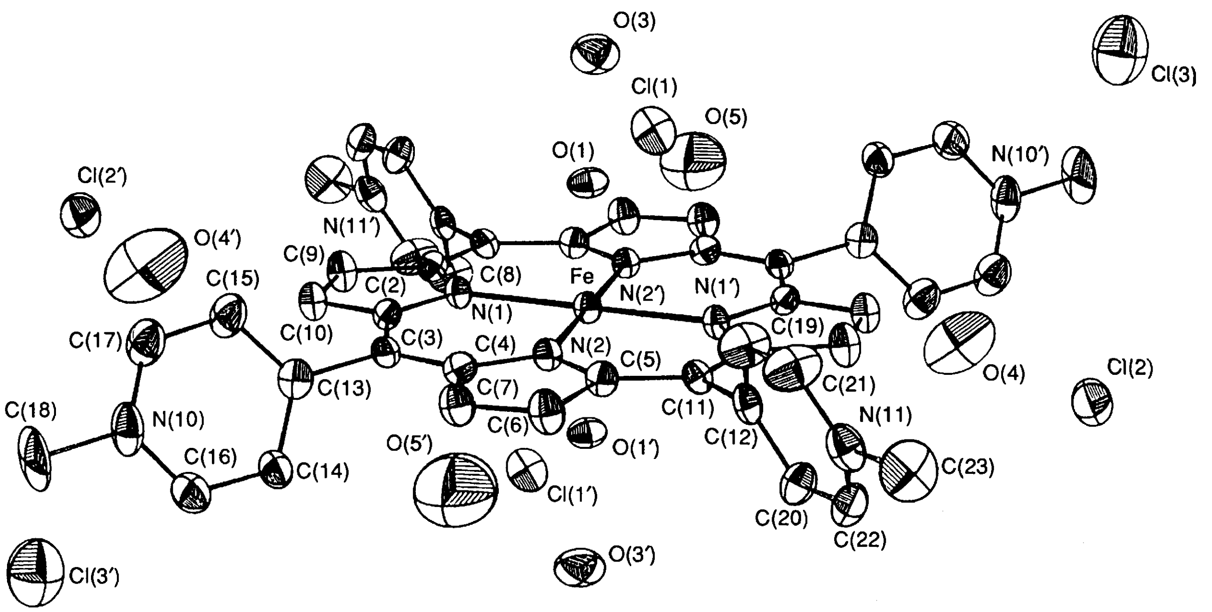

Fig. 1 An ORTEP plot of the non-hydrogen atoms in [Fe^{III}(tmpyp)]Cl$_5$·nH$_2$O. Atoms depicted as 38% probability ellipsoids. Non-carbon atoms are labelled with primes to indicate symmetry equivalence. For carbon atoms symmetry equivalents are not shown

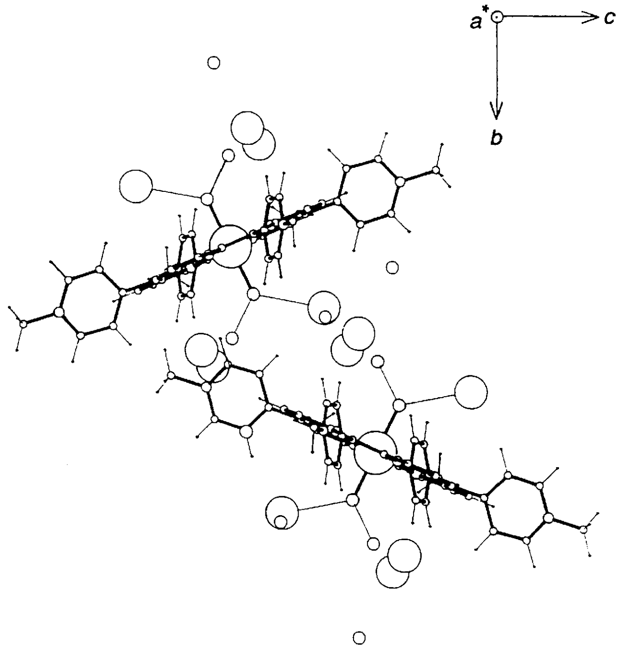

Fig. 2 Unit-cell contents of [Fe^{III}(tmpyp)]Cl$_5$·nH$_2$O showing the relative tilt of the porphyrins. Origin on upper Fe atom; Fe atoms separated by (0, 0.5, 0.5). Solvent–anion network: large circle, Cl$^-$; small circle, H$_2$O

Table 1 Atomic coordinates and site occupancy factors (s.o.f.s) for non-hydrogen atoms in [Fe^{III}(tmpyp)]Cl$_5$·nH$_2$O

Atom	*X/a*	*Y/b*	*Z/c*	s.o.f.
Fe[a]	0.0000	0.0000	0.0000	0.50
N(1)	−0.0719(5)	0.1379(5)	−0.0710(4)	1.00
N(2)	−0.1408(5)	−0.0747(5)	−0.0159(3)	1.00
N(10)	−0.5645(6)	0.1820(7)	−0.1993(5)	1.00
N(11)	0.1769(6)	0.5820(6)	−0.1141(5)	1.00
Cl(1)	0.0663(2)	0.3218(2)	0.1645(2)	1.00
Cl(2)	−0.3798(2)	0.4026(2)	−0.3465(2)	1.00
Cl(3)	−0.5973(4)	0.4430(5)	−0.1015(4)	0.75[b]
O(1)	−0.0079(4)	0.0790(4)	0.1135(3)	1.00
O(3)	−0.1469(6)	0.0069(6)	0.1853(4)	1.00
O(4)	−0.6148(9)	−0.0550(11)	−0.3512(6)	1.00
O(5)	−0.5171(11)	−0.3276(11)	−0.0582(8)	1.00
C(2)	−0.1751(6)	0.1548(6)	−0.1039(5)	1.00
C(3)	−0.2520(6)	0.0786(7)	−0.0958(5)	1.00
C(4)	−0.2349(6)	−0.0299(7)	−0.0573(5)	1.00
C(5)	−0.1586(6)	−0.1804(7)	0.0114(5)	1.00
C(6)	−0.2672(6)	−0.2016(7)	−0.0119(5)	1.00
C(7)	−0.3153(7)	−0.1094(7)	−0.0548(5)	1.00
C(8)	−0.0241(6)	0.2345(6)	−0.0868(5)	1.00
C(9)	−0.1023(7)	0.3159(7)	−0.1329(5)	1.00
C(10)	−0.1951(7)	0.2661(7)	−0.1425(5)	1.00
C(11)	0.0811(6)	0.2554(6)	−0.0604(5)	1.00
C(12)	0.1161(6)	0.3690(6)	−0.0810(5)	1.00
C(13)	−0.3638(7)	0.1159(7)	−0.1329(5)	1.00
C(14)	−0.4081(7)	0.1346(8)	−0.2211(6)	1.00
C(15)	−0.4240(7)	0.1317(7)	−0.0793(5)	1.00
C(16)	−0.5079(8)	0.1682(9)	−0.2510(6)	1.00
C(17)	−0.5242(7)	0.1646(8)	−0.1138(6)	1.00
C(18)	−0.6774(8)	0.2141(11)	−0.2355(8)	1.00
C(19)	0.1092(7)	0.3990(7)	−0.1636(5)	1.00
C(20)	0.1566(8)	0.4487(8)	−0.0150(6)	1.00
C(21)	0.1384(7)	0.5080(8)	−0.1799(5)	1.00
C(22)	0.1861(9)	0.5507(9)	−0.0333(6)	1.00
C(23)	0.2049(9)	0.7007(8)	−0.1337(8)	1.00

[a] Atom fixed upon special position. [b] This is equivalent to half a chloride ion and half a water molecule.

monomers, with exact molecular symmetry $\bar{1}$ (Figs. 1 and 2, Tables 1 and 2), and not as dimers. Although acid was not added to the recrystallisation mixture, it is likely that a trace of HCl from the preparation was present and this ensured that the porphyrin solutions were monomeric.[5,8] The porphyrin ring is planar and not saddle shaped or ruffled, as has been observed with some other metalloporophyrins.[5,9] Furthermore, the iron is six-co-ordinated and lies in the plane of the ring symmetrically bonded to two identical axial ligands. The crystal analysis clearly identifies a diaquairon(III) porphyrin structure and eliminates a five-co-ordinated species with a ligated chloride or an unsymmetrical aquachloro complex. The co-ordination of the axial water to a water of crystallisation as well as to a chloride ion and its bonding parameters (Table 3) exclude ligation of the iron(III) by OH$^-$. The core of the porphyrin ring is enlarged to accommodate the high-spin iron(III) atom. In agreement with this interpretation of the data, the measured Fe–N(porphyrin) [2.042(6) and 2.038(7) Å]

Table 2 Important bond lengths (Å) and angles (°) for $[Fe^{III}(tmpyp)]Cl_5 \cdot nH_2O$

N(1)–Fe	2.042(6)	N(2)–Fe–N(1)	90.0(3)
N(2)–Fe	2.038(7)	O(1)–Fe–N(1)	90.1(2)
O(1)–Fe	2.086(5)	O(1)–Fe–N(2)	90.1(2)
Cl(3) ••• N(10)	3.523(11)		
Cl(2) ••• $N(10^{II})$	3.477(10)		
Cl(3) ••• N(11)	3.409(10)		
Cl(1) ••• $N(11^{I})$	3.334(9)		

Symmetry operations applied: I $\bar{x}, \bar{y}, \bar{z}$: II $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$. NB Integral unit-cell translations not accounted for; *i.e.* ±1.0 have been added to fractional coordinates in the calculation of some bond lengths.

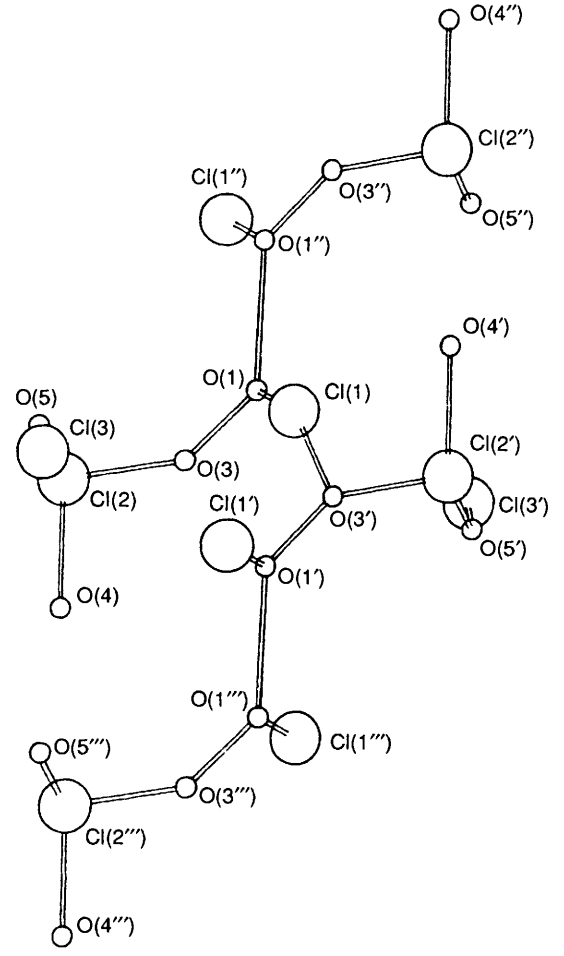

Fig. 3 Solvent–anion network for $[Fe^{III}(tmpyp)]Cl_5 \cdot nH_2O$. Symmetry-equivalent groups indicated by primes

Table 3 Bonding parameters (lengths in Å, angles in °) for the solvent–anion network

O(3) ••• O(1)	2.633(9)	O(1) ••• Cl(1) ••• $O(3^{II})$	148.1(3)
O(1) ••• Cl(1)	3.035(6)	$O(3^{I})$ ••• $Cl(2^{II})$ ••• O(4)	96.3(3)
$O(3^{II})$ ••• Cl(1)	3.183(10)	O(4) ••• $Cl(2^{II})$ ••• O(5)	117.6(3)
O(4) ••• $Cl(2^{II})$	3.258(11)	O(5) ••• $Cl(2^{II})$ ••• O(3)	128.0(3)
O(5) ••• $Cl(2^{II})$	3.198(12)	$O(4^{II})$ ••• Cl(3) ••• $O(5^{I})$	86.7(5)
$O(3^{I})$ ••• $Cl(2^{II})$	3.211(9)	$O(5^{I})$ ••• Cl(3) ••• O(5)	99.0(5)
O(5) ••• Cl(3)	2.892(16)	O(5) ••• Cl(3) ••• $O(4^{II})$	75.7(3)
$O(5^{I})$ ••• Cl(3)	2.903(16)	O(3) ••• O(1) ••• Cl(1)	113.6(2)
$O(4^{II})$ ••• Cl(3)	3.187(14)	Cl(1) ••• $O(3^{I})$ ••• $Cl(2^{II})$	115.8(3)
Cl(3) ••• $Cl(3^{I})$	3.766(12)	$Cl(2^{II})$ ••• $O(5^{I})$ ••• Cl(3)	125.8(4)

Symmetry operations as in Table 2.

and $Fe-O_{ax}$[2.086(5) Å] distances are identical to those reported by Scheidt *et al.*[10] for the diaqua complex of the non-polar iron(III) 5,10,15,20-tetraphenylporphyrin $[Fe^{III}(tpp)]$. The torsional angles for the *N*-methylpyridinio rings are 71.1° [C(8)–C(11)–C(12)–C(19)] and 63.4° [C(4)–C(3)–C(13)–C(15)]. These values are well above the minimum dihedral angles of approximately 60° observed for planar tpp-like structures.[9] Their exact value seems to be determined by the influence of the crystal packing and is presumably different in solution.

The complex $[Fe^{III}(tmpyp)]^{5+}$ crystallises with a monoclinic unit cell which does not belong to any of the families of crystal forms of tpp complexes summarised by Scheidt and Lee.[9] The crystal organisation also differs from that of the μ-oxo dimer of $Fe^{III}(tmpyp)$,[5] the metal-free H_2tmpyp^{4+},[11] and $[Fe^{III}(tpp)(H_2O)_2]ClO_4$.[10] This is due to the unique ligand structure of $[Fe^{III}(tmpyp)]^{5+}$ (Fig. 2 and Table 2). The five chloride counter ions are hydrogen-bonded to the nine water molecules in a cross-linked network of loosely interconnected 'daisy-chains' which interleaf between layers of porphyrin molecules (Fig. 3 and Table 3). One chloride, Cl(3), is only half occupied and the crystallographic data as well as the hydrogen-bonding pattern suggest that it shares the position with a water molecule. This necessarily introduces positional uncertainty also in O(4) and O(5), which are bonded to Cl(3), resulting in increased thermal parameters for these water oxygens.

Two chlorides per iron(III), Cl(1) and its symmetry-related counterpart, are associated with the metal *via* a water molecule [Cl ••• H_2O, 3.035(6) Å] each providing half of a charge. Furthermore, each pyridinium nitrogen on average makes contacts with $1\frac{1}{2}$ chlorides. These contact distances are slightly larger than the sum of the van der Waals radii for nitrogen and chlorine (3.3 Å)[12] (Table 2). It is clear from these results that individual charges on the metalloporphyrin are not directly associated with a single counter ion but rather the overall positive charge is balanced by that of the hydrogen-bonded anionic network.

Notwithstanding the formation of extensive solvent channels in the $[Fe^{III}(tmpyp)]^{5+}$ crystals, the packing of the porphyrin rings is markedly different from those recently described for the 'tetraarylporphyrin sponges'.[13] The porphyrin planes are not parallel, unlike the majority of other tetraarylporphyrins.[9] Instead, the planes enclose an angle of 47.9(8)° (Fig. 2). The chloride–water network and the addition of the methyl groups on the pyridine rings cause a wide separation of the porphyrin centres of 9.98(1) Å. This is 0.77 Å larger than the widest separation quoted by Scheidt and Lee.[9]

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