# COMMUNICATION

AN ANIONIC SIX-COORDINATE HIGH-SPIN IRON(III) PORPHYRIN

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<u>Abstract</u> - Isolation and characterisation of the tetrabutylammonium salt of difluoro iron(III) tetraphenylporphyrin are described.

All known iron(III) tetraphenylporphyrin compounds having a high spin (S = 5/2) ground state can be classified in two categories : (1) the well known neutral five-coordinate complexes of the type FeX(tpp), where X is an uninegative anion, and (2) the recently described cationic six-coordinate complexes  $[Fe(L)_2(tpp)]^+$ , in which L is an oxygen-donor molecule such as water, ethanol or dimethylsulfoxide<sup>1,2</sup>. We now report that axial ligation of iron(III) tetraphenylporphyrin by two fluoride anions gives rise to isolable anionic six-coordinate complexes in which the ferric ion is high-spin.

### EXPERIMENTAL

## Preparation of fluoro(tetraphenylporphyrinato) iron(III)

Tetraphenylporphyrin (H<sub>2</sub>tpp) was prepared by a literature method<sup>3</sup>. Direct insertion of the FeF<sup>2+</sup> molety from FeF<sub>3</sub> gave FeF(tpp) in a single step, a significant improvement with respect to previous methods<sup>4</sup>. H<sub>2</sub>tpp (3g) and FeF<sub>3</sub>.3H<sub>2</sub>O (1.5g) were dissolved in 1 l of dimethyl-formamide which had been dried over 4A molecular sieves for 4 days. The mixture was refluxed for 6 hours, and the solvent was then distilled off until a residual volume of ca. 200 ml was obtained. Overnight crystallisation gave the expected complex. After filtration and washing with ethanol, this crude product was dissolved in dichloromethane (200 ml) and recrystallised by slow addition of cyclohexane (300 ml). Yield : 3.17g (94 %). Found : C, 76.79 ; H, 4.19 ; N, 8.21 ; C<sub>44</sub>H<sub>28</sub>N<sub>4</sub>FeF requires C, 76.86 ; H, 4.10 ; N, 8.15. IR : 615 cm<sup>-1</sup> (v<sub>Fe=F</sub><sup>5</sup>).

### Preparation of tetrabutylammonium difluoro(tetraphenylporphyrinato)ferrate(III)

Addition of 150 mg of tetrabutylammonium fluoride trihydrate to 200 mg of FeF(tpp) in 15 ml of dichloromethane changed the colour of the solution from brown to green. Acetonitrile (30 ml) was then added, and the volume of the mixture was reduced to 10 ml with a rotating evaporator. The dark violet crystals which were obtained were filtered and dried in air. Yield : 220 mg (79 %). Found : C, 75.15 ; H, 6.80 ; N, 7.33 ; Fe, 5.97 ; F, 4.55. Calculated for  $[(C_4H_9)_4N]$  [FeF<sub>2</sub>( $C_{44}H_{28}N_4$ )] : C, 75.94 ; H, 6.80 ; N, 7.38 ; Fe, 5.88 ; F, 4.00. Electronic spectra were recorded on a Beckman Acta MVI spectrophotometer. Infrared spectra of KBr pellets were obtained on a Beckman 4250 instrument. A Varian E-104 A spectrometer was used for EPR spectra. Magnetic susceptibility measurements were made by the Faraday method.

### RESULTS AND DISCUSSION

Analytical data indicate that the anionic difluoro complex of iron(III) tetraphenylporphyrin can be isolated as a crystalline solid with a tetrabutylammonium counter ion. The formation of a similar complex of deuteroporphyrin IX in solution had been inferred by Momenteau, Mispelter, and Lexa on the basis of spectroscopic studies<sup>6</sup>.

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 $[NBu_4]$  [FeF<sub>2</sub>(tpp)] shows absorption maxima at 415,588, and 628 nm in dichloromethane solution. The Fe-F stretching frequency observed at 615 cm<sup>-1</sup> in FeF(tpp) is not found in the infrared spectrum of the difluoro complex. Instead, a broad, strong absorption is observed at 485 cm<sup>-1</sup>, which we assign to a trans F-Fe-F vibrational mode.

EPR spectra in frozen dichloromethane solution at 80 K show the usual pattern of high-spin iron(III) porphyrins :  $g_{\perp} = 5.7$ ,  $g_{//} = 2.0$ . In contrast to the report concerning the deuteroporphyrin IX complex<sup>6</sup>, we have not been able to detect a hyperfine splitting of the g = 2 line by the two fluorine nuclei of  $[FeF_2(tpp)]^-$ . Magnetic susceptibility measurements on the microcrystalline solid confirmed the S = 5/2 state : the value of the effective magnetic moment at room temperature is 5.95 BM.

The varied spin states of ferric porphyrins are known to be controlled by the nature and number of their axial ligands<sup>1</sup>. The present characterisation of  $[FeF_2(tpp)]^{-}$ , the first anionic six-coordinate ferric porphyrin with a high spin state, provides a further illustration of this concept. X-ray structure determination of this complex, crystallised as the 2-methyl-imidazolium salt<sup>7</sup>, confirms the trans difluoro configuration, and it shows a planar, radially expanded porphyrin core with long iron-nitrogen bond distances  $(2.064(3)\text{\AA})$ , as expected for a high spin iron(III) porphyrin complex<sup>1</sup>.

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