Iron(III) Porphyrin Sulphate Complexes. Total Assignment of the Carbon-13 N.M.R. Spectrum

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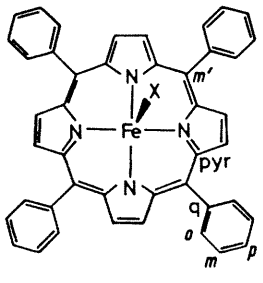
Summary Synthesis and physical characterization, including ^{13}C n.m.r. measurements, are reported for the first iron(III) porphyrin sulphate species.

THE spin state of iron(III) porphyrins is dictated by whether the axial ligands are weak-field or strong-field. Weak ionic ligands usually give rise to high-spin five-co-ordinate species in which the iron atom is displaced *ca.* 0·5 Å from the porphyrin plane. Perchlorate complexes constitute a notable exception, however, for which case both solid-state[1] and solution[2] measurements are consistent with a quantum-mechanically admixed $S = 3/2, 5/2$ state. This report describes the first iron(III) porphyrin sulphate complex, which is only the second example of an iron (III) porphyrin complex having a dianionic counter ion; the other is the μ-oxo-bridged dimer.

In a typical preparation, to a solution of 100 mg of iron(III) μ-oxo-bis-5,10,15,20-tetraphenylporphyrin, $(FeTPP)_2O$, in 30 ml of methylene chloride, an equivalent amount of 6 M aqueous sulphuric acid was added. An excess of acid must be avoided or the bisulphate derivative will be formed. The mixture was shaken for at least 15 min, and the methylene chloride layer evaporated to dryness, and vacuum dried for 12 h. Dissolution of the solid in the minimum amount of toluene and slow addition of heptane resulted in needle-like crystals which were vacuum dried at 100 °C. Elemental analysis showed a ratio of one sulphur to two iron atoms (S 2·33%, Fe 7·76%). The visible–u.v. spectrum in methylene chloride at 1×10^{-5} M is that of a high-spin iron(III) porphyrin. Absorption bands were found at: 680 (ϵ 2·9 l mmol^{-1} cm^{-1}), 576 (3·5), 508 (11·0), 407·5 (113), 372 (51), and 347 nm (43). Solution magnetic moment measurements in chloroform over the temperature range 228—327 K yielded an invariant μ_{eff} of $5{\cdot}6 \pm 0{\cdot}1$ B.M. No e.s.r. signals were observed at 77 K for a 2 mM frozen methylene chloride–toluene solution.

Both ^1H and ^{13}C n.m.r. spectra have been recorded for the sulphate derivatives. A most unusual feature of the spectra is the relatively small linewidths. Thus, the pyrrole proton linewidth at half height in $CDCl_3$ at 26 °C for FeTPP·Cl is *ca.* 250 Hz, whereas in FeTPP·1/2(SO_4) it is 74 Hz. Broad ^{13}C resonances and low sensitivity allowed earlier observation of only the phenyl carbon resonances of FeTPP·Cl.[3] Mispelter *et al.*[4] have reported and reassigned the *meso*-carbon resonance using ^{13}C-labelled



FeTPP ½(SO$_4$)

FeTPP I However, these authors were unable to detect the pyrrole carbon signals We have now located two additional signals for FeTPP 1/2(SO$_4$) in a far downfield region at 1216 and 1257 p p m (26 °C) as shown in the Figure Other assignments are consistent with those published by Mispelter *et al*[4] Based on linewidth differences it is reasonable to assign the 1257 p p m peak to the α- and the 1216 p p m peak to the β-pyrrole carbon atoms Resonances followed approximately Curie law behaviour The sharper peak is also detectable at 1123 p p m in the iodide derivative of FeTPP(*p*-OMe) using our Bruker HX-90E instrument Observation of both very broad pyrrole signals in this spectral region was possible for FeTPP Cl when a very short pulse recovery time was used (50 μs for the JEOL FX-90Q)

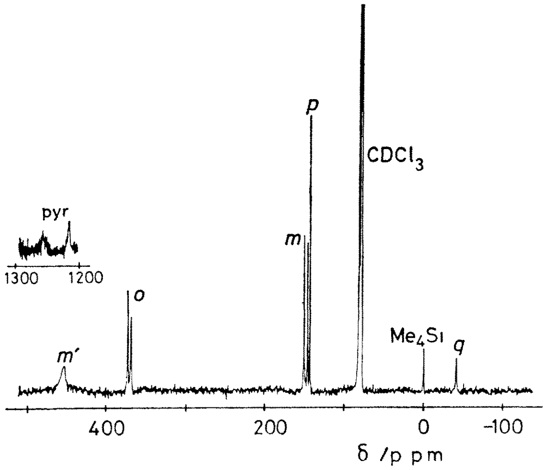


FIGURE ^{13}C N m r spectrum at 22 6 MHz (CDCl$_3$, Me$_4$Si) of 0 05 M FeTPP 1/2(SO$_4$) at 26 °C Downfield pyrrole resonances are shown separately in the upper left for clarity Relative peak intensities are distorted by a non-uniform power distribution in the 41 7 KHz spectrum, by rapid pulsing (ten times per second), and by sensitivity enhancement techniques which increase linewidths by 5 Hz

Visible–u v and ^{1}H and ^{13}C n m r spectra, cyclic voltammetry,[7] and magnetic susceptibility studies lead to the conclusion that FeTPP 1/2(SO$_4$) is an essentially high-spin iron(III) species However, the compound is unusual in having a relatively short electronic relaxation time as judged by sharp n m r signals and absence of e s r signals Configuration interaction of the $S = 5/2$ state with a higher energy $S = 3/2$ state *via* spin–orbit coupling is not a likely mechanism of inducing electronic relaxation, as the n m r resonances for $S = 3/2, 5/2$ spin admixed species are not particularly sharp[2] Also, sulphate should be a better ligand than perchlorate, making the $S = 3/2$ state much less accessible A large value for the zero-field splitting would be predicted to yield well resolved n m r resonances, but a relatively small difference in the *ortho*-carbon resonance positions does not follow the trend observed for other high-spin iron(III) porphyrins where this difference is proportional to zero-field splitting[6] Owing to the dianionic nature of sulphate, a bridged dimeric structure might be expected, where the antiferromagnetic exchange interaction is very weak In this model the sulphate bridge provides a mechanism for electronic relaxation by either a through-space or through-bond interaction

Other physical characterization including low temperature magnetic measurements, Mossbauer work, and *X*-ray crystallography will be required to resolve the unusual electronic relaxation properties of FeTPP 1/2(SO$_4$)

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