Alkane (or Arene)-sulphinato and -sulphonato-iron(III) Porphyrins: Synthesis and Physicochemical Properties; Crystal Structure of Benzenesulphinato(5,10,15,20-tetraphenylporphyrinato)iron(III) †

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Sulphinatoiron(III) porphyrins [FeL(SO$_2$R)] (L = porphyrinate, R = alkyl or aryl) have been prepared by the insertion reaction of sulphur dioxide into the Fe–C σ bond of alkyl(or aryl)iron(III) porphyrins [FeLR]. The obtained products are easily oxidised by molecular oxygen to the corresponding sulphonate derivatives, also generated by acid hydrolysis of the Fe–O bonds of the μ-oxo-dimers [(FeL)$_2$O] by the appropriate sulphonic acid. The stereochemistry of the metal centre has been established by ^{1}H n.m.r., e.s.r., and i.r. measurements and confirmed by the crystal structure determination of the title compound by *X*-ray diffraction methods. The crystals are triclinic, space group *P*1, with a = 11.01(2), b = 11.09(1), c = 11.37(2) Å, α = 107.2(1), β = 107.9(1), γ = 110.2(1)°, and Z = 1. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares calculations to R = 0.097 for 1 901 reflections. The iron atom is five-co-ordinated by the four nitrogen atoms of the porphyrin and one oxygen atom of the sulphinato-group [Fe–O 1.92(1) Å].

It is well established that the spin state and stereochemistry of the iron centre in both protein and model compounds are almost entirely determined by the number and the nature of the axial ligands.[1] In the case of iron(III) synthetic porphyrins, co-ordination of weak-field anionic ligands leads to high-spin ($S = \frac{5}{2}$) five-co-ordinate complexes where the metal is displaced out of the four-nitrogen plane of the porphyrin (0.39—0.54 Å).[2] Stronger-field ligands, commonly electron-donating, such as pyridine or imidazole, lead to low-spin *trans*-six-co-ordinate species with the iron essentially in the porphyrin plane.[2] The crystal structures of some high-spin *trans*-six-co-ordinate metalloporphyrins have also been reported;[3-5] in these cases the iron atom is centred in the porphyrin plane involving expansion of the macrocycle core. Finally iron(III) porphyrins co-ordinated with ClO_4^- exhibit a quantum-admixed $S = \frac{3}{2},\frac{5}{2}$ state with the metal atom displaced 0.26—0.28 Å out of the four-nitrogen plane.[6,7]

Co-ordination of iron(III) by oxyanionic ligands usually generates high-spin complexes. In this case the stereochemistry of the metal centre is controlled by the nature of the axial ligand. Acetato-[8] and methoxo-complexes[9] are five-co-ordinated with the metal displaced 0.485(2) and 0.484(1) Å respectively from the four-nitrogen plane, and the nitrato-derivative[10] is *cis*-six-co-ordinated with the metal–four-nitrogen plane distance equal to 0.53 Å. According to their ^{1}H n.m.r. characteristics, arenesulphonatoiron(III) porphyrins[10] seem also to be high-spin *cis*-six-co-ordinated, and sulphato-derivatives[10] are high-spin dimeric species bridged by a SO_4^{2-} anion. Sulphinatoiron(III) porphyrins have not yet been reported.

In a recent paper[11] we pointed out a series of new highly oxygen-sensitive alkyliron(III) porphyrins [FeLR] (1; L = oep, tpp, tmtp, or tptp; R = alkyl) ‡ with unusual characteristics. These complexes and their aryliron(III) analogues[12] are five-co-ordinated and exhibit ^{1}H n.m.r. spectra typical of low-spin iron(III) porphyrins.[13] On the basis of magnetic measurements, Ogoshi *et al.*[14] suggested the same stereochemistry and spin state for the iron centre of a series of aryliron(III) octaethylporphyrins.

Such complexes with a metal–carbon σ bond can undergo insertion reactions with small molecules. In order to study their chemical reactivity, but also in an attempt to synthesise the unknown iron(III) sulphinate derivatives in the porphyrinic series, we treated complexes (1) dissolved in toluene with sulphur dioxide. The reaction afforded new five-co-ordinate high-spin species characterised as [FeL(SO$_2$R)], (2; R = alkyl or aryl), which are rapidly oxidised by molecular oxygen to [FeL(SO$_3$R)], (3). The latter products are high-spin iron(III) porphyrins, identical to those resulting from the acid hydrolysis of the μ-oxo-bridged dimers [(FeL)$_2$O], (4), with the appropriate sulphonic acid.

In this paper we report the synthesis and properties of the complexes (2) and (3) and their characterisation on the basis of elemental analysis, mass, ^{1}H n.m.r., e.s.r., i.r., and u.v.–visible spectroscopic data. An *X*-ray study carried out on the complex [Fe(tpp)(SO$_2$C$_6$H$_5$)] allowed us to correlate the spin state and stereochemistry of the iron(III) centre with the magnetic properties shown by these complexes.

Experimental

Iron(III) porphyrins were prepared as the σ-alkyl or σ-aryl derivatives according to the methods that we have previously reported,[11,12] or as the μ-oxo-dimers by literature methods.[15,16]

Preparation of the [FeL(SO$_2$R)] *Compounds* (2).—A solution

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† *Supplementary data available* (No. SUP 23805, 23 pp.): thermal parameters, H-atom co-ordinates, least-squares planes, ligand dimensions, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. units employed: eV ≈ 1.60 × 10^{-19} J; B.M. ≈ 9.27 × 10^{-24} A m^2; Oe = $10^3/4\pi$ A m^{-1}.

‡ Abbreviations: oep = 2,3,7,8,12,13,17,18-octaethylporphyrinate(2–); tpp = 5,10,15,20-tetraphenylporphyrinate(2–); tmtp = 5,10,15,20-tetra-*m*-tolylporphyrinate(2–); tptp = 5,10,15,20-tetra-*p*-tolylporphyrinate(2–).

Table 1. Experimental data and yields

Complex	Recrystallisation solvent [a]	Yield (%)	Analysis (%) [b]				
			C	H	N	S	Fe
(2a) [Fe(oep)(SO_2CH_3)]	A–B (2 : 1)	42	66.7 (66.55)	7.0 (7.1)	8.4 (8.4)	4.8 (4.8)	8.6 (6.35)
(2b) [Fe(oep)($SO_2C_6H_5$)]	A–B (2 : 1)	90	69.1 (69.1)	6.8 (6.8)	7.7 (7.65)	4.4 (4.4)	7.6 (7.65)
(2c) [Fe(tpp)(SO_2CH_3)]	A–C (1 : 1)	40	71.8 (72.3)	4.5 (4.2)	6.8 (7.5)	3.6 (4.3)	7.1 (7.45)
(2d) [Fe(tpp)($SO_2C_6H_5$)]	A–B (1 : 1)	47	73.8 (74.15)	4.1 (4.1)	6.6 (6.9)	3.8 (3.95)	6.9 (6.9)
(2e) [Fe(tmtp)(SO_2CH_3)]	A–C (1 : 3)	80	72.7 (73.2)	4.6 (4.9)	7.0 (6.95)		6.9 (6.95)
(2f) [Fe(tmtp)($SO_2C_6H_5$)]	A–B (1 : 2)	25	76.0 (74.9)	4.8 (4.8)	6.8 (6.45)		6.8 (6.45)
(2g) [Fe(tptp)(SO_2CH_3)]	A–C (3 : 2)	40	72.3 (73.2)	5.1 (4.9)	6.7 (6.95)		6.9 (6.95)
(2h) [Fe(tptp)($SO_2C_6H_5$)]	A–B (1 : 2)	75	75.5 (74.9)	4.9 (4.8)	6.0 (6.45)		6.5 (6.45)
(3a) [Fe(oep)(SO_3CH_3)]	A–D (1 : 1)	40	64.8 (65.0)	6.9 (6.95)	8.2 (8.2)	4.6 (4.7)	8.8 (8.2)
(3b) [Fe(oep)($SO_3C_6H_5$)]	A–D (1 : 1)	75	67.1 (67.6)	6.5 (6.65)	7.9 (7.5)	4.0 (4.3)	7.6 (7.5)
(3c) [Fe(tpp)(SO_3CH_3)]·$0.5C_6H_6$	E–D (1 : 1)	60	72.1 (71.8)	4.3 (4.3)	6.8 (7.0)	3.5 (4.0)	7.0 (6.95)
(3d) [Fe(tpp)($SO_3C_6H_5$)]	A–D (1 : 1)	85	72.4 (72.7)	4.0 (4.05)	6.8 (6.8)	3.7 (3.9)	7.3 (6.75)
(3e) [Fe(tmtp)(SO_3CH_3)]	A–B (1 : 2)	46	71.9 (71.8)	5.0 (4.8)	6.9 (6.85)	3.2 (3.9)	6.8 (6.8)
(3f) [Fe(tmtp)($SO_3C_6H_5$)]	A–B (1 : 2)	50	73.6 (73.55)	4.7 (4.7)	6.3 (6.35)	3.7 (3.65)	6.3 (6.35)
(3g) [Fe(tptp)(SO_3CH_3)]	A–D (3 : 2)	40	71.8 (71.8)	4.9 (4.8)	6.6 (6.85)	3.4 (3.9)	6.7 (6.8)
(3h) [Fe(tptp)($SO_3C_6H_5$)]	A–D (1 : 1)	50	73.2 (73.55)	5.0 (4.7)	6.3 (6.35)	3.4 (3.65)	5.2 (6.35)

[a] A = Toluene; B = n-heptane; C = n-pentane; D = n-hexane; E = benzene. [b] Calculated values are given in parentheses.

of well dried [FeLR], (1) (0.35 mmol), in toluene (50 cm^3) freshly distilled over sodium and oxygen-free was cooled to −18 °C. A weak flow of sulphur dioxide was bubbled through the solution for 30 min with stirring, then the solution was allowed to warm to room temperature. After evaporation of the solvent *in vacuo* the crude material was recrystallised under a dry argon atmosphere.

Oxidation of Complexes (2) *by Molecular Oxygen to give* [FeL(SO_3R)], (3).—A weak flow of dry oxygen was passed through a solution of [FeL(SO_2R)], (2) (0.35 mmol), in toluene (50 cm^3) for a few minutes at room temperature. The solvent was then removed under reduced pressure and the residual solid was recrystallised.

Preparation of the [FeL(SO_3R)], (3), *by Acid Hydrolysis of the* [$(FeL)_2O$] *Derivatives* (4).—A mixture of the μ-oxo-dimer [$(FeL)_2O$] (0.35 mmol) and an excess of sulphonic acid in dry toluene (250 cm^3) was heated at 110 °C during 15—30 min. The reaction was monitored by u.v.–visible spectroscopy. After completion of the reaction the solution was cooled and then introduced into a separating funnel. The excess of acid was eliminated and the remaining organic layer washed three times with distilled water without shaking so that hydrolysis of the iron–sulphonate bond(s) would not occur. After drying the solution over magnesium sulphate and evaporating the solvent *in vacuo*, the crude product was recrystallised.

The reaction conditions, yields, and elemental analyses for complexes (2) and (3) are given in Table 1.

Physical Measurements.—Elemental analyses were performed by The Service de microanalyse du C.N.R.S. Mass spectra were obtained in the electron-impact mode with a Finnigan 3300 spectrometer: ionising energy, 30—70 eV; ionising current, 0.4 mA; source temperature, 250—400 °C. Nuclear magnetic resonance spectra were recorded in the pulse Fourier-transform mode with use of a JEOL FX 100 instrument. One hundred scans over 16 K points were accumulated for each spectrum at 294 ± 1 K. Samples (6 mg) were dissolved in C_6D_6 or $CDCl_3$ (0.5 cm^3) and chemical shifts are reported with respect to internal $SiMe_4$. Electron spin resonance spectra were obtained with a Varian E4 *Q*-band spectrometer in toluene solution at 115 K. Infrared spectra were recorded on a Perkin-Elmer 580 B apparatus. Samples were prepared as 1% dispersions in CsI pellets or Nujol mulls. Electronic absorption spectra were recorded on a Perkin-Elmer 559 spectrophotometer using 5×10^{-3} mol l^{-1} toluene solutions. Magnetic measurements were performed on a superconducting quantum interference device, with a field of 10 000 Oe.

Crystal and Molecular Structure Determination.—*Crystal data.* [Fe(tpp)($SO_2C_6H_5$)], $M = 809$, triclinic, space group $P1$, $a = 11.01(2)$, $b = 11.09(1)$, $c = 11.37(2)$ Å, $\alpha = 107.2(1)$, $\beta = 107.9(1)$, $\gamma = 110.2(1)^\circ$, $U = 1\,108$ Å^3, $Z = 1$, $D_c = 1.21$ g cm^{-3}, $F(000) = 387$, λ(Cu-K_α) = 1.542 42 Å, μ(Cu-K_α) = 35 cm^{-1}; crystal size 0.2 × 0.3 × 0.2 mm.

Data collection. Black crystals were obtained by recrystallisation of the complex from toluene–n-heptane (1 : 1). In

Table 2. Fractional co-ordinates of the non-hydrogen atoms (100 K) in [Fe(tpp)($SO_2C_6H_5$)]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Fe	0.9628	0.7273	0.8614	C(40)	1.060(1)	1.232(1)	1.086(1)
N(1)	0.891(1)	0.831(1)	0.982(1)	C(41)	1.988(1)	1.287(1)	1.019(1)
N(2)	1.040(1)	0.907(1)	0.830(1)	C(42)	1.024(1)	1.434(1)	1.091(1)
N(3)	0.952(1)	0.616(1)	0.675(1)	C(43)	1.133(1)	1.516(2)	1.221(2)
N(4)	0.811(1)	0.537(1)	0.830(1)	C(44)	1.206(1)	1.463(1)	1.290(1)
C(1)	0.811(1)	0.768(1)	1.039(1)	C(45)	1.170(1)	1.319(1)	1.228(1)
C(2)	0.815(1)	0.877(1)	1.152(2)	C(50)	1.175(1)	0.858(1)	0.557(1)
C(3)	0.899(1)	1.008(1)	1.151(1)	C(51)	1.107(2)	0.871(2)	0.451(2)
C(4)	0.941(1)	0.975(1)	1.043(1)	C(52)	1.170(1)	0.906(1)	0.359(1)
C(5)	1.022(1)	1.078(1)	1.012(1)	C(53)	1.308(2)	0.918(2)	0.394(2)
C(6)	1.079(1)	1.050(1)	0.916(1)	C(54)	1.381(1)	0.903(1)	0.506(1)
C(7)	1.164(1)	1.150(1)	0.886(1)	C(55)	1.316(2)	0.871(2)	0.588(2)
C(8)	1.191(1)	1.075(1)	0.784(1)	C(60)	0.786(1)	0.213(1)	0.564(1)
C(9)	1.107(1)	0.921(1)	0.743(1)	C(61)	0.870(2)	0.158(2)	0.638(2)
C(10)	1.105(1)	0.817(1)	0.638(1)	C(62)	0.830(2)	0.011(2)	0.574(2)
C(11)	1.029(1)	0.668(1)	0.609(1)	C(63)	0.718(1)	−0.078(1)	0.438(1)
C(12)	1.027(1)	0.551(1)	0.502(1)	C(64)	0.648(2)	−0.020(2)	0.370(2)
C(13)	0.954(1)	0.431(1)	0.505(1)	C(65)	0.680(1)	0.126(1)	0.436(1)
C(14)	0.903(1)	0.464(1)	0.607(1)	C(70)	0.664(1)	0.590(1)	1.089(1)
C(15)	0.824(1)	0.366(1)	0.644(1)	C(71)	0.736(1)	0.568(1)	1.209(1)
C(16)	0.777(1)	0.402(1)	0.741(1)	C(72)	0.669(2)	0.536(2)	1.282(2)
C(17)	0.685(2)	0.291(2)	0.770(2)	C(73)	0.530(1)	0.522(1)	1.253(1)
C(18)	0.656(1)	0.360(1)	0.867(1)	C(74)	0.457(1)	0.536(1)	1.136(1)
C(19)	0.731(1)	0.507(1)	0.903(1)	C(75)	0.526(1)	0.570(1)	1.061(1)
C(20)	0.745(1)	0.628(1)	1.006(1)	Fe′	0.884(1)	0.728(1)	0.799(1)
S	1.265 6(6)	0.727 3(6)	1.012 6(6)	S′	0.584(2)	0.713(2)	0.641(2)
O(1)	1.125(1)	0.738(1)	1.000(1)	O′(1)	0.700(2)	0.697(2)	0.649(2)
O(2)	1.247(1)	0.622(1)	0.887(1)	O′(2)	0.619(2)	0.818(2)	0·771(2)
C(30)	1.370(2)	0.895(2)	1.030(2)	C′(30)	0.490(2)	0.563(2)	0.628(2)
C(31)	1.371(1)	1.022(1)	1.098(1)	C′(31)	0.523(2)	0.454(2)	0.554(2)
C(32)	1.453(2)	1.147(2)	1.120(2)	C′(32)	0.415(2)	0.317(2)	0.527(2)
C(33)	1.580(2)	1.169(2)	1.085(2)	C′(33)	0.310(2)	0.295(2)	0.575(2)
C(34)	1.588(2)	1.056(2)	1.014(2)	C′(34)	0.330(2)	0.438(2)	0.650(2)
C(35)	0.480(2)	0.902(2)	−0.015(2)	C′(35)	0.398(2)	0.560(2)	0.665(2)

order to study the space group and also to find a crystal suitable for *X*-ray measurements, several crystals of [Fe(tpp)($SO_2C_6H_5$)] were mounted in thin-walled glass capillaries. However, the reflection profiles were very broad and the signal-to-noise ratio was optimised by collection of data at 100 ± 5 K. The diffraction intensities were collected on a four-circle Enraf–Nonius diffractometer using a θ—2θ scan technique and Cu-K_α radiation. Each reflection was scanned from $2\theta(K_{\alpha_1}) - 1.5$ to $2\theta(K_{\alpha_2}) + 1.5$. Three standard reflections measured every 2 h showed a monotonic decline in intensity reaching 20% at the end of data collection. A linear fit of the three standard reflections was used to correct the data. A total of 2 882 reflections was measured in half of the diffraction sphere with $2 < \theta < 53°$, and 1 901 reflections having $\sigma(I) < 0.3I$ were used to solve and refine the structure. The intensities were corrected for Lorentz and polarisation effects, but not for absorption.

Solution and refinement. The crystal structure was solved by direct methods using the MULTAN program [17] which gave in space group $P1$ the co-ordinates of the iron, nitrogen, and some carbon atoms of the porphyrin ring. Fourier synthesis then gave the positions of the atoms of the sulphinato-group and all the non-hydrogen atoms (R = 0.18). At this stage a careful study of the difference electron-density maps showed a large residual peak of 2.8 e Å^{-3} located at fractional co-ordinates (0.87, 0.72, 0.79) below the porphyrinato-plane at about 0.95 Å from the iron atom. This peak was interpreted as a partial iron atom resulting from disorder in the molecular packing, and explained the broadness of the reflection profiles. This type of disorder has also been found in [Fe(tpp)Cl].[18] Furthermore this assumption was verified by the location of a second sulphinato-group linked to the second iron atom. Another Fe($SO_2C_6H_5$) moiety was then included in the least-squares refinement. The sum of the occupancies of both Fe($SO_2C_6H_5$) groups was constrained to 1. It was impossible to determine the co-ordinates of the corresponding second porphyrinato-group. The hydrogen-atom positions were calculated and included in the structure-factor calculations. Each non-hydrogen atom was refined anisotropically. The final values of the discrepancy indices obtained with the SHELX program [19] are R = 0.097 and R' = 0.099; goodness of fit = 1.96. The rather high value of the agreement factors is easily explained by the poor quality of the crystals due to the disorder in the molecular packing. At the end of the refinement the partial occupation of the two Fe($SO_2C_6H_5$) groups was 0.810(1) and 0.190(1). A three-dimensional model of the crystal was built to verify that the second sulphinato-group has enough room to lie in the unit cell. A final Fourier map did not reveal any residual electron density at the expected position of the third ligand oxygen atom. Thus the complex was not oxidised during the data collection.

Final positional parameters are listed in Table 2, selected bond distances and angles in Table 3.

Results and Discussion

The sulphonatoiron(III) porphyrins [FeL(SO_3R)], (3), were obtained by two different methods: (*a*) insertion of a SO_2 molecule into the Fe–C σ bond of [FeLR], (1), followed by oxidation with molecular oxygen of the resulting sulphinate derivatives (2), or (*b*) by acid hydrolysis of the Fe–O bonds of the μ-oxo-bridged dimers [$(FeL)_2O$], (4) (Scheme 1). The

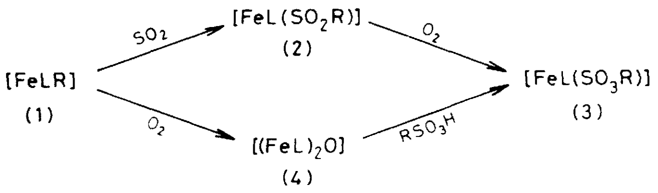
Table 3. Selected bond distances (Å) and angles (°) in the molecule and standard deviations

Iron co-ordination		Ligand			
Fe–N(1)	2.05(2)	S–O(1)	1.56(2)	C(32)–C(33)	1.53(2)
Fe–N(2)	2.07(1)	S–O(2)	1.46(2)	C(33)–C(34)	1.32(3)
Fe–N(3)	2.05(1)	S–C(30)	1.73(2)	C(34)–C(35)	1.57(3)
Fe–N(4)	2.03(1)	C(30)–C(31)	1.38(2)	C(30)–C(35)	1.44(3)
Fe–O(1)	1.92(1)	C(31)–C(32)	1.26(2)		

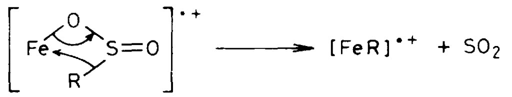
Macrocycle							
N(1)–N(2)	2.83(2)	C(3)–C(4)	1.43(2)	C(13)–C(14)	1.45(2)	C(9)–C(10)	1.39(2)
N(2)–N(3)	2.81(2)	C(4)–C(5)	1.39(2)	C(14)–C(15)	1.39(2)	N(4)–C(16)	1.38(2)
N(3)–N(4)	2.82(2)	C(1)–C(20)	1.34(2)	N(2)–C(6)	1.42(2)	N(4)–C(19)	1.41(2)
N(4)–N(1)	2.86(2)	N(3)–C(11)	1.38(2)	N(2)–C(9)	1.41(2)	C(15)–C(16)	1.37(2)
N(1)–C(1)	1.37(2)	N(3)–C(14)	1.44(2)	C(5)–C(6)	1.42(2)	C(16)–C(17)	1.50(2)
N(1)–C(4)	1.36(2)	C(10)–C(11)	1.45(2)	C(6)–C(7)	1.39(2)	C(17)–C(18)	1.34(2)
C(1)–C(2)	1.47(2)	C(11)–C(12)	1.48(2)	C(7)–C(8)	1.39(2)	C(18)–C(19)	1.40(2)
C(2)–C(3)	1.44(2)	C(12)–C(13)	1.32(2)	C(8)–C(9)	1.47(2)	C(19)–C(20)	1.42(2)

Iron co-ordination		Ligand			
O(1)–Fe–N(1)	101.2(6)	Fe–O(1)–S	137.7(9)	O(1)–S–C(30)	99.0(9)
O(1)–Fe–N(2)	107.6(5)	O(1)–S–O(2)	113.8(7)	O(2)–S–C(30)	106.9(9)
O(1)–Fe–N(3)	105.5(6)				
O(1)–Fe–N(4)	96.2(5)				

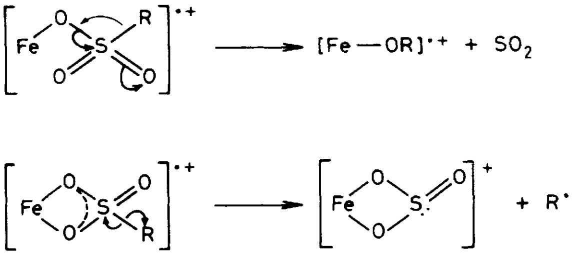
Macrocycle					
C(1)–N(1)–Fe	123(1)	C(12)–C(11)–C(10)	122(1)	N(2)–C(9)–C(8)	108(1)
C(4)–N(1)–Fe	126(1)	C(11)–C(12)–C(13)	107(2)	N(2)–C(9)–C(10)	130(1)
C(1)–N(1)–C(4)	110(1)	C(12)–C(13)–C(14)	108(1)	C(8)–C(9)–C(10)	121(2)
N(1)–C(1)–C(2)	110(1)	N(3)–C(14)–C(13)	111(1)	C(16)–N(4)–Fe	126(1)
N(1)–C(1)–C(20)	127(1)	N(3)–C(14)–C(15)	123(1)	C(19)–N(4)–Fe	130.5(9)
C(2)–C(1)–C(20)	122(2)	C(13)–C(14)–C(15)	126(1)	C(16)–N(4)–C(19)	103(1)
C(1)–C(2)–C(3)	103(1)	C(4)–C(5)–C(6)	125(1)	N(4)–C(16)–C(15)	128(1)
C(2)–C(3)–C(4)	109(1)	C(9)–C(10)–C(11)	119(2)	N(4)–C(16)–C(17)	110(1)
N(1)–C(4)–C(3)	108(1)	C(6)–N(2)–Fe	128(1)	C(15)–C(16)–C(17)	122(1)
N(1)–C(4)–C(5)	128(2)	C(9)–N(2)–Fe	125(1)	C(16)–C(17)–C(18)	107(1)
C(3)–C(4)–C(5)	124(1)	C(6)–N(2)–C(9)	105(1)	C(17)–C(18)–C(19)	107(2)
C(11)–N(3)–Fe	128.7(8)	N(2)–C(6)–C(5)	121(1)	N(4)–C(19)–C(18)	114(1)
C(14)–N(3)–Fe	127(1)	N(2)–C(6)–C(7)	112(2)	N(4)–C(19)–C(20)	116(1)
C(11)–N(3)–C(14)	102(1)	C(5)–C(6)–C(7)	127(1)	C(18)–C(19)–C(20)	130(2)
C(11)–N(3)–C(14)	102(1)	C(6)–C(7)–C(8)	107(1)	C(14)–C(15)–C(16)	124(1)
N(3)–C(11)–C(10)	126(1)	C(7)–C(8)–C(9)	107(1)	C(1)–C(20)–C(19)	131(2)
N(3)–C(11)–C(12)	112(1)				



Scheme 1. R = Alkyl or aryl



Scheme 2.



Scheme 3.

latter complexes are also degradation products of compounds (1) in the presence of molecular oxygen.

In most of the mass spectra of complexes (2) the molecular peak when observed corresponds to the protonated form (Table 4). Its intensity is very low (0.02—1.95%) and traces of oxygen in the ionisation chamber lead to the $[M - O]^+$ or $[M + OH]^+$ ions. The parent peak corresponds to $[M - SO_2R]^+$ or $[M - SO_2R + H]^{\cdot+}$, however we also observed the fragments $[M - SO_2]^{\cdot+}$ or $[M - SO_2 + H]^+$ resulting from the elimination of SO_2 without previous fission of the SO_2–R bond according to a four-centre cyclic mechanism (Scheme 2). This mechanism has already been reported for alkane- or arene-sulphinatoindium(III) porphyrins [20] and is characteristic of unidentate *O*-bonded sulphinate.[21] Complexes (3) show similar fragmentation patterns (Table 4). However, the intensity of their molecular peak is higher (4.72—100%) and $[M - SO_2]^{\cdot+}$ and $[M - R]^+$ ions are observed. These fragments could be explained by the pathways shown in

Table 4. Characteristic mass spectral and i.r. data

Complex	I.r. (cm^{-1}) ν_{asym} (SO$_2$)	I.r. (cm^{-1}) ν_{sym} (SO$_2$)	I.r. (cm^{-1}) $\Delta\nu$	Mass spectra *m/e*	Mass spectra Relative intensity	Mass spectra Fragmentation pattern
(2a)	1 106	857	249	667	0.68	$M^{\cdot +}$
				603	1.71	$[M - SO_2]^{\cdot +}$
				588	100.00	$[M - SO_2CH_3]^{\cdot +}$
(2b)	1 111	848	263	745	1.42	$[M + O]^+$
				730	1.07	$[M + H]^+$
				589	100.00	$[M - SO_2C_6H_5 + H]^{\cdot +}$
(2c)	1 109	921	188	749	0.09	$[M + 2\ H]^{\cdot +}$
				683	1.85	$[M - SO_2]^{\cdot +}$
				668	100.00	$[M - SO_2CH_3]^+$
(2d)	1 111	865	246	826	5.85	$[M + OH]^+$
				745	6.91	$[M - SO_2]^{\cdot +}$
				668	100.00	$[M - SO_2C_6H_5]^+$
(2e)	1 110	841	269	804	0.05	$[M + H]^+$
				739	13.19	$[M - SO_2]^{\cdot +}$
				725	100.00	$[M - SO_2CH_3]^+$
(2f)	1 115	862	253	882	4.61	$[M + OH]^+$
				802	9.23	$[M - SO_2 + H]^+$
				726	100.00	$[M - SO_2C_6H_5 + 2\ H]^+$
(2g)	1 109	836	273	803	0.93	$[M + H]^+$
				738	14.95	$[M - SO_2]^{\cdot +}$
				724	100.00	$[M - SO_2CH_3]^+$
(2h)	1 110	869	241	882	5.17	$[M + OH]^+$
				802	5.17	$[M - SO_2 + H]^+$
				724	100.00	$[M - SO_2C_6H_5]^+$

Complex	I.r. (cm^{-1}), ν(SO$_3$)						Mass spectra *m/e*	Mass spectra Relative intensity	Mass spectra Fragmentation pattern
(3a)	1 299	1 200	1 158	1 048	994		684	32.10	$[M + H]^+$
							589	100.00	$[M - SO_3CH_3 + H]^{\cdot +}$
(3b)	1 302	1 212	1 165	1 028	970		746	100.00	$[M + H]^+$
							588	73.64	$[M - SO_3C_6H_5]^+$
(3c)	1 302	1 200	1 152	1 046	975	944	748	4.72	$[M - CH_3]^+$
							702	59.84	$[M - SO_2 + 3\ H]^+$
							667	100.00	$[M - SO_3CH_3 - H]^{\cdot +}$
(3d)	1 305,	1 210	1 168	1 087		953	827	8.73	$[M + 2\ H]^{\cdot +}$
	1 310						748	2.91	$[M - C_6H_5]^+$
							668	100.00	$[M - SO_3C_6H_5]^+$
(3e)	1 309	1 200	1 156	1 046	976	945	804	5.47	$[M - CH_3]^+$
							758	60.27	$[M - SO_2 + 3\ H]^+$
							723	100.00	$[M - SO_3CH_3 - H]^{\cdot +}$
(3f)	1 305,	1 210	1 165			995	883	10.00	$[M + 2\ H]^{\cdot +}$
	1 310						804	4.11	$[M - C_6H_5]^+$
							725	100.00	$[M - SO_3C_6H_5 + H]^{\cdot +}$
(3g)	1 306	1 202	1 157	1 046	977	946	818	7.24	$[M - H]^+$
							804	7.24	$[M - CH_3]^+$
							758	60.86	$[M - SO_2 + 3\ H]^+$
							723	100.00	$[M - SO_3CH_3 - H]^{\cdot +}$
(3h)	1 305	1 210	1 168	1 072		958	883	11.27	$[M + 2H]^{\cdot +}$
							804	6.99	$[M - C_6H_5]^+$
							725	100.00	$[M - SO_3C_6H_5 + H]^{\cdot +}$

Scheme 3, repectively involving either a unidentate or a bidentate sulphonate group. Mass spectral data consequently do not allow us to suggest an unambiguous stereochemistry for the iron centre of compounds (3).

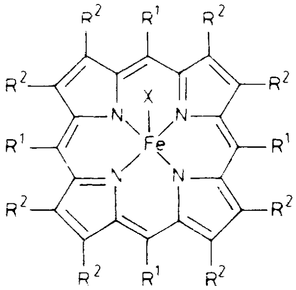
Alkyl or aryl groups behave as strong-field ligands leading to low-spin $S = \frac{1}{2}$ five-co-ordinate [FeLR] complexes.[12] The insertion of SO$_2$ or SO$_3$ between the metal and the carbon atoms displaces the iron farther away from the mean porphyrin plane so that splitting of the *d*-orbital levels of the metal is diminished. Consequently, occupancy of the d_{z^2} and the $d_{x^2-y^2}$ orbitals by unpaired electrons occurs and typical ^{1}H n.m.r. spectra of high-spin $S = \frac{5}{2}$ species are observed for complexes (2) and (3) (Table 5). In particular, the resonance of the pyrrole protons in the tetra-aryl porphyrinate complexes appears around 80 and 76.5 p.p.m. downfield from internal SiMe$_4$ for compounds (2) and (3) with linewidths close to 350 and 250 Hz respectively. Both the out-of-the-porphyrin-plane displacement of the iron atom and the asymmetry of the axial ligand render the two sides of the macrocycle magnetically non-equivalent,[22] so that *m*-protons are highly anisotropic in the limit of slow phenyl-group rotation (which is the case at 294 K) giving rise to two different peaks around 11.5 and 12.5 p.p.m. Similar splittings are observed for the methyl protons of the *m*-tolylporphyrinate complexes (Table 5). Strong dipolar interactions induce considerable broadening of the *o*-proton signals so that they are not observed.

The out-of-plane displacement of the iron ion in these high-spin species is also clearly demonstrated by the doubling of the α-CH$_2$ peak of octaethylporphyrinate derivatives (Table 5). However, the methylenic protons of the sulphonate complexes are more diastereotopic ($\Delta\delta = 5$ p.p.m.) than those of the sulphinate complexes suggesting a greater displacement of the metal centre in the former. This assumption is in accordance with the upfield shift of the pyrrole proton resonance of tetra-arylporphyrinatoiron(III) sulphonates with respect to their corresponding sulphinate derivatives. Phillippi *et al.*[10] on the basis of *X*-ray diffraction and ^{1}H n.m.r. data for five-co-ordinate [Fe(tpp)Cl] and *cis*-six-co-ordinate [Fe(tpp)(NO$_3$)] high-spin complexes pointed out that the greater the displacement of the iron atom from the porphyrin plane the less downfield was the pyrrole proton signal. They consequently suggested a *cis*-six-co-ordination for the products [Fe(tpp)(SO$_3$C$_6$H$_5$)] and [Fe(tpp)(SO$_3$C$_6$H$_4$CH$_3$-*p*)]. The ^{1}H n.m.r. characteristics of compounds (2) and (3) are in good agreement with their observations and allow us to propose unidentate sulphinate bonding in compounds (2) and *cis*-six-co-ordination for the corresponding sulphonate derivatives (3).

Resonance signals for the axial ligand protons are not observed. Nevertheless a broad peak between 17 and 19 p.p.m. for the compounds [FeL(SO$_2$C$_6$H$_5$)] and at 12.2 p.p.m. for complex [Fe(oep)(SO$_3$C$_6$H$_5$)] might be attributed to the *m*-protons of the phenyl group.

E.s.r. spectra with axial symmetry ($g_\perp \approx 6$ and $g_\parallel \approx 2$) are obtained for complexes (2) and (3) (Table 6) confirming their high-spin $S = \frac{5}{2}$ state.[23] Similarly with the acetatoiron(III) porphyrins [FeL(CO$_2$CH$_3$)][8] and iron(III) 'porphodimethenes'[24] rhombicity is not observed, although these complexes do not exhibit a four-fold symmetry. A thermo-

Table 5. Proton n.m.r. data[a]



X = SO_2R: (2)
X = SO_3R: (3)

Compound	R^1	R^2	R	Protons of R^1			Protons of R^2			Protons of R		
					multiplicity, intensity	δ		multiplicity, intensity	δ		multiplicity, intensity	δ
(2a)	H	CH_2CH_3	CH_3		s, 4	−43[b]	β-CH_3	s, 24	5.85		*c*	
							α-CH_2	s, 8	37.2			
							α′-CH_2	s, 8	39.3			
(2b)	H	CH_2CH_3	C_6H_5		s, 4	(−41)[d]	β-CH_3	s, 24	6.10 (6.10)	*o*-H		*c*
							α-CH_2	s, 8	39.4 (44.1)	*m*-H	s, 2	17.5 (17.0)
							α′-CH_2	s, 8	40.4 (44.5)	*p*-H		*c*
								s, 8	79.9[e]		*c*	
(2c)	C_6H_5	H	CH_3	*o*-H		*c*						
				m-H	s, 4	11.42						
				m′-H	s, 4	12.40						
				p-H	s, 4	6.85						
(2d)	C_6H_5	H	C_6H_5	*o*-H		*c*		s, 8	79.8	*o*-H		*c*
				m-H	s, 4	11.55				*m*-H	s, 2	18.2
				m′-H	s, 4	12.52				*p*-H		*c*
				p-H	s, 4	6.77						
(2e)	C_6H_4Me-*m*	H	CH_3	*o*-H		*c*		s, 8	79.5		*c*	
				m-H	s, 2	11.24						
				m′-H	s, 2	12.22						
				m-CH_3	s, 6	2.82						
				m′-CH_3	s, 6	2.93						
				p-H	s, 4	6.60						
(2f)	C_6H_4Me-*m*	H	C_6H_5	*o*-H		*c*		s, 8	80.4	*o*-H		*c*
				m-H	s, 2	10.91				*m*-H	s, 2	19.3
				m′-H	s, 2	11.82				*p*-H		*c*
				m-CH_3	s, 6	3.49						
				m′-CH_3	s, 6	3.56						
				p-H	s, 4	6.34						
(2g)	C_6H_4Me-*p*	H	CH_3	*o*-H		*c*		s, 8	79.5		*c*	
				m-H	s, 4	11.42						
				m′-H	s, 4	12.42						
				p-CH_3	s, 12	5.82						
(2h)	C_6H_4Me-*p*	H	C_6H_5	*o*-H		*c*		s, 8	79.8	*o*-H		*c*
				m-H	s, 4	11.02				*m*-H	s, 2	19.2
				m′-H	s, 4	11.90				*p*-H		*c*
				p-CH_3	s, 12	5.42						
(3a)	H	CH_2CH_3	CH_3		s, 4	−47	β-CH_3	s, 24	6.80		*c*	
							α-CH_2	s, 8	42.4			
							α′-CH_2	s, 8	47.5			
(3b)	H	CH_2CH_3	C_6H_5		s, 4	(−39)[d]	β-CH_3	s, 24	6.68	*o*-H		*c*
							α-CH_2	s, 8	42.3	*m*-H		12.2
							α′-CH_2	s, 8	47.2	*p*-H		*c*
(3c)	C_6H_5	H	CH_3	*o*-H		*c*		s, 8	77.0[f]		*c*	
				m-H	s, 4	11.63						
				m′-H	s, 4	12.7						
				p-H	s, 4	6.54						
(3d)	C_6H_5	H	C_6H_5	*o*-H		*c*		s, 8	76.5		*c*	
				m-H	s, 4	11.75						
				m′-H	s, 4	12.84						
				p-H	s, 4	6.53						

[a] Spectra recorded in C_6D_6 at 21 °C with $SiMe_4$ as internal reference; chemical shifts downfield from $SiMe_4$ are defined as positive. s = Singlet. [b] At 308 K. [c] Not observed. [d] Values from spectra recorded in $CDCl_3$ are given in parentheses. [e] Linewidth: 350 Hz. [f] Linewidth: 250 Hz.

Table 5 (*continued*)

				Protons of R¹			Protons of R²		Protons of R	
Compound	R¹	R²	R		multiplicity, intensity	δ	multiplicity, intensity	δ	multiplicity, intensity	δ
(3e)	C_6H_4Me-*m*	H	CH_3	*o*-H		*c*	s, 8	76.2	*c*	
				m-H	s, 2	11.71				
				m′-H	s, 2	12.78				
				m-CH_3	s, 6	2.34				
				m′-CH_3	s, 6	2.71				
				p-H	s, 4	6.39				
(3f)	C_6H_4Me-*m*	H	C_6H_5	*o*-H		*c*	s, 8	76.2	*c*	
				m-H	s, 2	11.70				
				m′-H	s, 2	12.79				
				m-CH_3	s, 6	2.35				
				m′-CH_3	s, 6	2.75				
				p-H	s, 4	6.40				
(3g)	C_6H_4Me-*p*	H	CH_3	*o*-H		*c*	s, 8	76.9	*c*	
				m-H	s, 4	11.68				
				m′-H	s, 4	12.80				
				p-CH_3	s, 12	5.85				
(3h)	C_6H_4Me-*p*	H	C_6H_5	*o*-H		*c*	s, 8	76.3	*c*	
				m-H	s, 4	11.84				
				m′-H	s, 4	12.90				
				p-CH_3	s, 12	5.94				

Table 6. E.s.r. and u.v.–visible spectroscopic data

	E.s.r.		U.v.–visible (λ/nm) [a]								
				Soret							
Complex	$g_\perp$	$g_\parallel$		I	II						
(2a)	6.09	*b*		360 (93.4)	397 (149)	500 (9.6)	528 [c] (11.3)	572 (5.3)	619 (8.4)		
(2b)	6.32	2.10		375 (57.3)	393 (58.6)	498 (6.1)	533 (5.7)	582 (3.2)	623 (2.3)		
(2c)	6.13	2.06		345 (23.4)	412 (111)	505 (6.8)		570 (2.3)	613 (0.4)	646 (0.6)	674 (0.7)
(2d)	6.32	*b*		350 (18.5)	411 (66.4)			570 (4.4)	611 (2.0)		674 (0.5)
(2e)	6.17	1.99		350 (42.2)	412 (146)	505 (12.9)		570 (8.4)	611 (3.7)		665 (1.4)
(2f)	6.39	*b*		350 (30.4)	410 (114)	500 (7.7)		571 (7.1)	612 (3.0)	650 (0.9)	675 (0.6)
(2g)	6.11	2.04		350 (50.5)	416 (177)	500 (16.2)		572 (8.3)	613 (4.2)		670 (1.3)
(2h)	6.32	2.01		355 (32.9)	415 (107)	499 (9.4)		571 (4.2)	611 (1.8)	646 (1.4)	675 (1.0)
(3a)	6.19	2.07		377 (87.8)	391 (88.6)	502 (8.0)	532 (8.2)	574 (sh)	632 (4.4)		
(3b)	6.14	2.05		381 (92.4)	391 (91.9)	504 (8.8)	534 (8.6)	573 (3.5)	636 (4.2)		
(3c)	6.13	2.00	343 (34.1)	374 (45.7)	412 (115)	507 (11.2)		572 (2.9)	649 (2.0)		682 (2.2)
(3d)	6.26	1.99	348 (37.6)	378 (51.6)	414 (123)	509 (11.0)		574 (2.3)	654 (6.8)		680 (6.8)
(3e)	6.23	2.00	343 (38.2)	374 (51.7)	413 (117)	508 (11.4)		574 (2.7)	652 (2.1)		684 (2.2)
(3f)	6.26	2.01	345 (41.0)	375 (54.8)	415 (140)	510 (12.6)		571 (2.5)	651 (0.8)		587 (0.7)
(3g)	6.21	2.02	343 (33.9)	374 (46.5)	413 (114)	509 (11.0)		573 (2.9)	652 (1.7)		687 (2.1)
(3h)	6.15	2.00	352 (40.0)	382 (55.6)	415 (129)	510 (11.7)		574 (1.9)	655 (0.2)		686 (0.3)

[a] $10^{-3}\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ given in parentheses. sh = Shoulder. [b] Not observed. [c] Also 556 nm (ε 5 700 $dm^3\ mol^{-1}\ cm^{-1}$).

magnetic study of [Fe(tpp)($SO_2C_6H_5$)], which follows a Curie law between 4 and 300 K, gave $\mu_{eff.}$ = 5.88 B.M.

Electronic spectra of complexes (2) and (3) are similar to those of other high-spin iron(III) porphyrins and belong to the hyperclass.[25,26] They show one or two extra bands in the visible region and another one {compounds (2) and [Fe(oep)(SO_3R)]} or two [all compounds (3) except oep derivatives] blue shifted with respect to the Soret band (Table 6). The hyper character is more pronounced for the octaethylporphyrinate complexes, the intensities of bands I and II (see

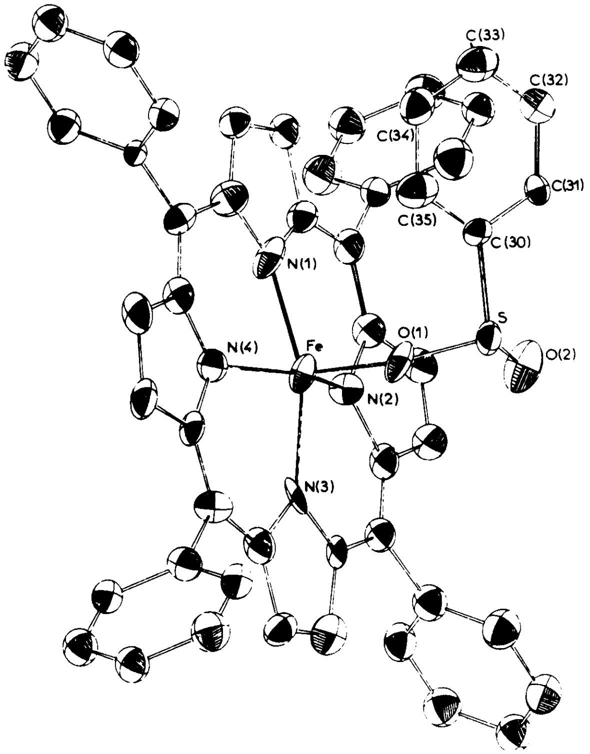


Figure. ORTEP view of [Fe(tpp)($SO_2C_6H_5$)] with the main sulphonato-group

Table 6) being of the same magnitude for these complexes. The greater electron donicity of the oep macrocycle compared to the tetra-arylporphyrins is probably responsible for this behaviour.

Infrared spectroscopy is a powerful tool in the structural characterisation of metallic sulphinates and sulphonates. The location [27-29] and wavenumber separation [30] of the symmetrical and asymmetrical vibrations of the SO_2 group depend on the nature of the metal-sulphinate linkage. For complexes (2), $\nu_{sym}(SO_2)$ and $\nu_{asym}(SO_2)$ appear between 840 and 1 100 cm^{-1} with $240 < \Delta\nu < 270$ cm^{-1} (Table 4) suggesting a unidentate *O*-sulphinato-arrangement. The sulphonate structure is also confirmed for compounds (3) by the position and intensity of the SO_3 bands.[31,32] However a choice between an *O* and an *O,O'* mode is difficult since the bands due to the latter are broad and often overlap with those of the porphyrin skeleton.

The above assumptions are fully confirmed by the *X*-ray diffraction results obtained for the complex [Fe(tpp)(SO_2-C_6H_5)]. The Figure shows an ORTEP [33] view of [Fe(tpp)-($SO_2C_6H_5$)] with the main sulphinato-group. The co-ordination polyhedron of the iron is of the 4 : 1 type in accord with *O*-sulphinato-bonding. The iron atom lies 0.45(2) Å from both four-nitrogen and porphyrinato-planes. The mean Fe-N distance 2.05(2) ± 0.02 Å is in good agreement with the average value (2.065 Å) given by Reed *et al.*[34] for an iron(III) high-spin centre. The Fe-O bond length [1.92(1) Å] is statistically equal to that [1.898(3) Å] observed in [Fe(tmtp)(O_2-CCH_3)] [8] but slightly longer than that found in [Fe(tpp)-(OCH_3)].[9] However, this iron-sulphinate distance is much shorter than the corresponding distance in [In(tpp)(SO_3CH_3)] [2.35(1) Å] [20] where the ionic character of the complex is well established. The metal-oxygen-sulphur bond angle [137.7(9)°] is the same as that observed in the above structure [136.7(6)°].

The sulphinato-group, linked to the metallic atom by oxygen O(1), exhibits two different S-O bond distances [1.46(2) and 1.56(2) Å]. The shorter bond corresponds to O(2) which is not bound to the iron [O(2) $\cdots$ Fe 3.66(2) Å]. The phenyl-sulphur distance is normal [S-C(30) 1.73(2) Å].

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