Spectral and Electrochemical Anion Sensing by a Novel 5,10,15,20-Tetrakis(R-substituted) Porphyrin Receptor (R ◻ C₆H₄NHC(O)C₅H₄CoC₅H₅⁺ PF₆⁻)

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A novel 5,10,15,20-tetrakis(R-substituted) porphyrin receptor molecule (R = C₆H₄NHC(O)C₅H₄CoC₅H₅⁺ PF₆⁻) **3** is prepared and is shown to spectrally and electrochemically sense halide, nitrate, hydrogen sulfate and dihydrogen phosphate guest anions.

The molecular recognition of anionic guest species of biochemical, medical and environmental importance is an area of intense current interest.[1] Of the classes of abiotic anion receptors reported to date, however, very few have the capability of sensing anions *via* optical[2] and/or electrochemical[3] means. The porphyrin macrocycle is a well-known photo- and redox-active moiety which, because of its neutrality at or near physiological pH, cannot itself bind anions.[4] This contrasts with the family of expanded porphyrins which, in their protonated forms under the same pH conditions, can complex halide and phosphate anions.[5] In an attempt to produce, to our knowledge, the first porphyrin-based anion receptor we describe here the synthesis and preliminary anion coordination investigations of a novel 5,10,15,20-tetrakis(R-substituted)porphyrin molecule [R = C₆H₄NHC(O)C₅H₄CoC₅H₅⁺ PF₆⁻] that binds and spectrally and electrochemically senses, through respective perturbations of the receptor's porphyrin Soret band and both organometallic and porphyrin redox couples, halide, nitrate, hydrogen sulfate and dihydrogen phosphate anionic guest species.

The condensation of an excess amount of chlorocarbonyl cobaltocenium chloride **1**[6] and *cis*-α,α,α,α-atropisomer 5,10,15,20-tetrakis(2-aminophenyl)porphyrin **2**[7] in dry acetonitrile–dimethyl formamide in the presence of triethylamine

initially gave a crude product which was purified by Sephadex LH30 column chromatography using acetonitrile as the eluent. Addition of excess ammonium hexafluorophosphate precipitated the novel *cis*-5,10,15,20-tetrakis(R-substituted) porphyrin receptor (R = C₆H₄NHC(O)C₅H₄CoC₅H₅⁺ PF₆⁻, **3**) in 45% yield (Scheme 1). A similar synthetic procedure was followed with excess chlorocarbonyl ferrocene and **2** to prepare the ferrocene analogue **4** in 75% yield.† The reaction of zinc acetate and **4** in a dichloromethane–methanol solvent mixture gave the zinc complex **5** in quantitative yield. Crystals of **5** suitable for X-ray crystallographic investigation were obtained from methanol–chloroform solution.‡

The molecule is shown in Figs. 1(*a*) and (*b*) which are, respectively, projections through the porphyrin plane and perpendicular to it. The zinc atom is bonded to the four nitrogen atoms of the porphyrin at distances of 2.041(7), 2.044(6), 2.048(7) and 2.091(8) Å and to a methanol molecule at 2.091(8) Å. The metal atom is 0.27 Å above the plane of the four nitrogen atoms towards the methanol oxygen atom.
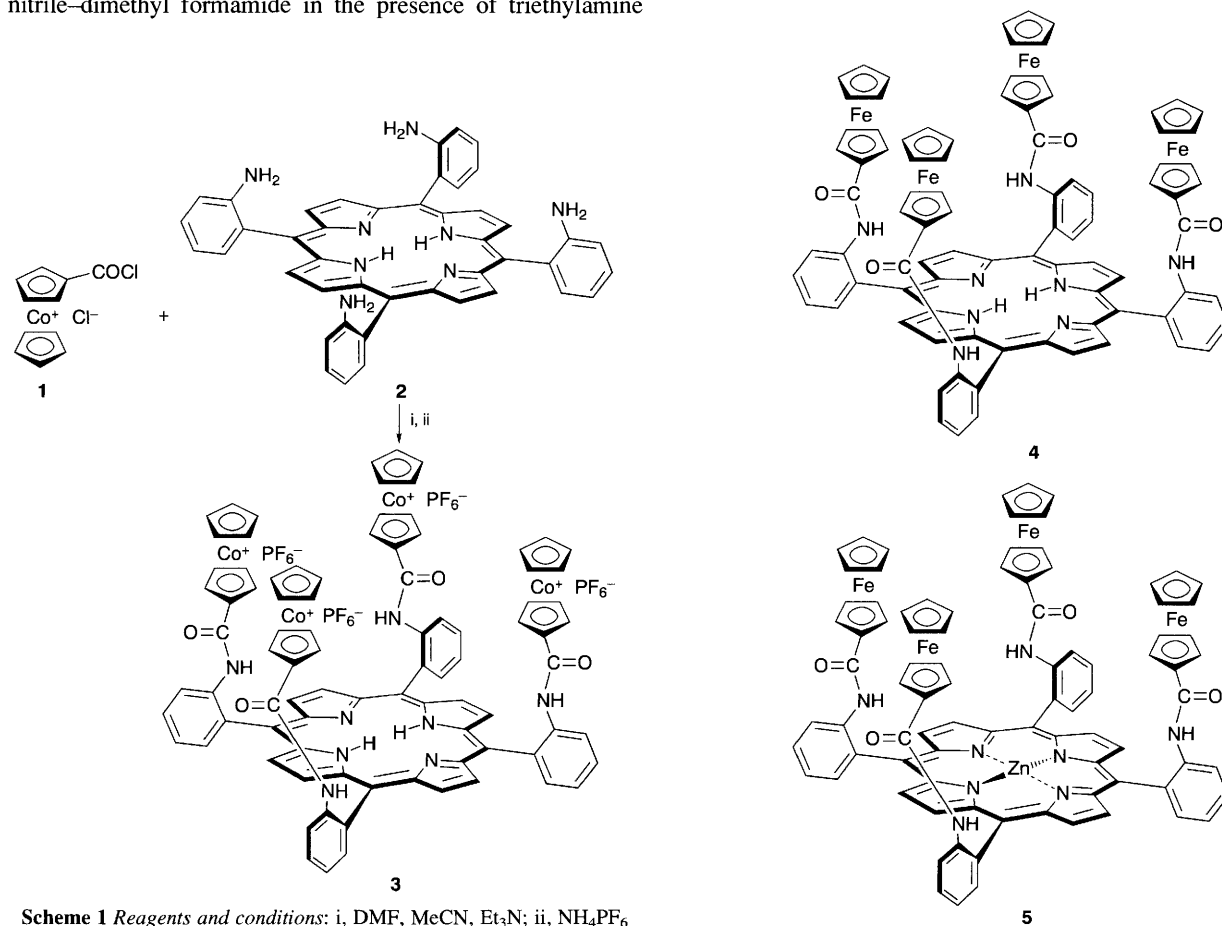
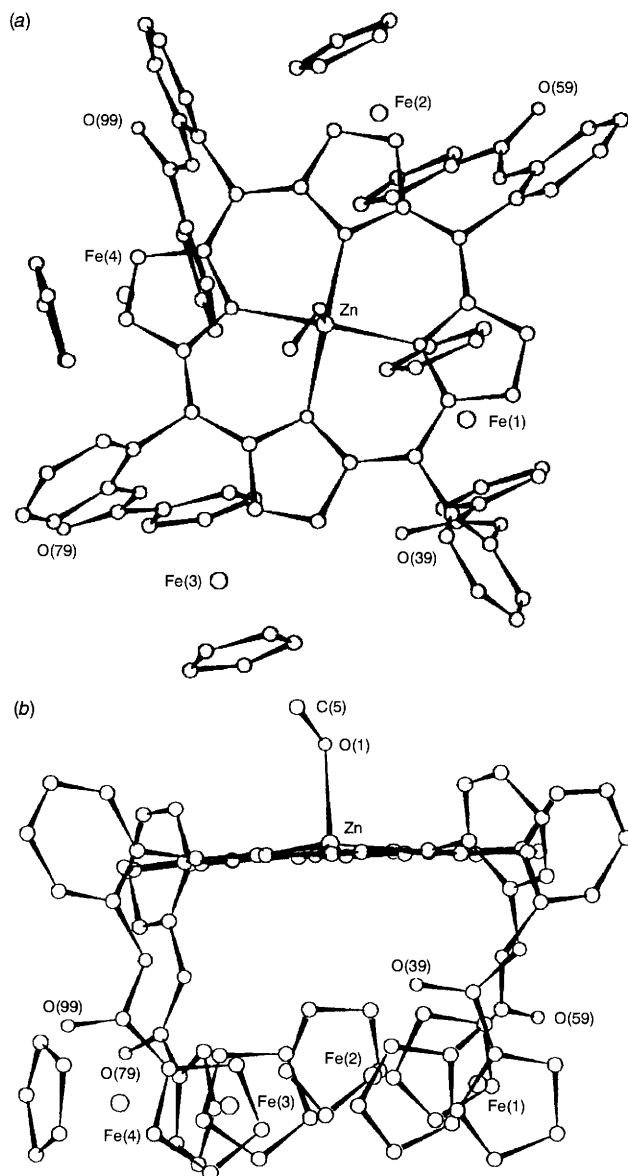**Scheme 1** *Reagents and conditions:* i, DMF, MeCN, Et₃N; ii, NH₄PF₆

(a)

(b)

Fig. 1 Structure of **5**: projections (a) through and (b) perpendicular to the porphyrin plane

Table 1 Stability constant data for **3** and anions in CD₃CN

Anion	K^a/dm³ mol⁻¹
Cl⁻	860
Br⁻	820
NO₃⁻	190

^{a} Errors estimated to be ≤ 10%.

The four phenyl rings intersect this plane of four nitrogen atoms at angles of 71.9, 68.7, 83.5 and 74.9°, respectively. There is a significant difference between the positions of one of the carbonyl oxygen atoms and the other three, thus O(39) is directed into the cavity, and the other three [O(59), O(79), O(99)] are directed outwards.

Evidence for anion recognition initially came from ¹H NMR titration studies. The addition of tetrabutylammonium halides, nitrate, hydrogen sulfate and dihydrogen phosphate to deu-

Table 2 Electrochemical data^a of **3** and its electrochemical anion recognition properties

	Porphyrin oxidation/V	Porphyrin reduction/V	Cobaltocenium reduction/V
3	+0.75^b	−1.24, −1.60	−1.50^c
ΔE(Cl⁻)/mV^d	15	<5, <5	40
ΔE(Br⁻)/mV^d	10	<5, <5	35
ΔE(NO₃⁻)/mV^d	5	<5, <5	5
ΔE(HSO₄⁻)/mV^d	50	<5, <5	75
ΔE(H₂PO₄⁻)/mV^d	75	<5, <5	225

^{a} Obtained in acetonitrile solution containing 0.2 mol dm⁻³ NBu₄BF₄ as supporting electrolyte. Solutions were ca. 1 × 10⁻³ mol dm⁻³ in receptor and potentials were determined with reference to an Ag/Ag⁺ electrode. ^{b} Two-electron process. ^{c} Four-electron process. ^{d} Cathodic shift in redox wave produced by presence of anions (up to five equiv.) added as their tetrabutylammonium salts.

teriated acetonitrile ¹H NMR solutions of **3** resulted in substantial perturbations of the receptor's protons. For example, with Cl⁻ the amide, cyclopentadienyl and pyrrole protons shifted downfield by up to 0.7 ppm. In all cases the resulting titration curves suggest a 1:1, **3**: X⁻ stoichiometry. The computer program EQNMR[8] was used to estimate the stability constants from the ¹H NMR titration data for selected anions§ and the results are summarised in Table 1.

Compared to the quantitative anion coordination investigations with simple monosubstituted arylamide cobaltocenium receptors,[9] these stability constant values are much larger, by at least an order of magnitude, which suggests positive cooperativity of anion binding via favourable amide hydrogen bonding and electrostatic interactions by the four cobaltocenium moieties of **3**. The pronounced selectivity preference for the halide anions over nitrate is also noteworthy. Disappointingly, analogous ¹H NMR anion coordination studies with the neutral ferrocene porphyrin derivative **4** revealed only relatively small perturbations of the receptor's protons (Δδ < 0.05 ppm). However, predictably the zinc complex **5** does from 1:1 stoichiometric complexes with anions in deuteriated dichloromethane solutions.

Experimental evidence for the electronic energy levels of the porphyrin moiety of **3** being able to sense the nearby coordination of anionic guest species initially came from UV–VIS spectroscopic studies. In acetonitrile solution the Soret band of **3** (λmax 425 nm) was significantly bathochromically shifted on addition of H₂PO₄⁻ (Δλ = 15 nm), hypsochromically shifted with Cl⁻ (Δλ = 10 nm) and split into two maxima (λ = 430, 440 nm) with HSO₄⁻.¶ The electrochemical properties of **3** were investigated by cyclic and square-wave voltammetries (Table 2). The porphyrin redox chemistry exhibited by **3** is typical of a 'picket fence' porphyrin,[10] a two-electron oxidation at 0.75 V and two one-electron reduction waves at −1.24 and −1.60 V. All four cobaltocenium moieties of **3** are reduced at the same potential (Table 2). Cyclic voltammograms were also recorded after progressively adding stoichiometric equivalents of anion guests to the electrochemical solutions, and the results are also summarised in Table 2. Significant one-wave cathodic shifts of the porphyrin oxidation wave and the poly(cobaltocenium) redox couple of **3** are observed with all anionic guest species except NO₃⁻, the complexed anion effectively stabilises the respective oxidised redox components of **3**.‖ Interestingly, the porphyrin reduction waves of **3** are not significantly perturbed with any anionic guest. It is noteworthy, as observed with monosubstituted cobaltocenium derivatives,[9] H₂PO₄⁻ produces the largest magnitude of cathodic shifts. The syntheses of related porphyrin-based anion receptors are currently under study.

Footnotes

† All new compounds were fully characterised by elemental analyses, ^{1}H and ^{13}C NMR and FAB-MS.

‡ *Crystal data* for 5·2MeOH·CHCl$_3$, formula $C_{92}H_{86}C_{13}Fe_4N_8O_7Zn$, M = 1810.81, monoclinic, $P2_1/n$, a = 12.924(11), b = 21.177(13), c = 29.193(22) Å, β = 94.48(1)°, U = 7965.5 Å^3, Z = 4, D_c = 1.510 Mg m^{-3}, μ = 1.173 mm^{-1}, $F(000)$ 3740, 23305 reflections were collected up to 2θ of 50° of which 13323 were independent, [R(int)] = 0.080. The structure was solved by direct methods and refined by full-matrix least-squares techniques (all non-hydrogen atoms anisotropic) on F^2 to a conventional R of 0.0786 for the 7868 reflections above background [$I > 2\sigma(I)$]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Anion complexes with HSO$_4^-$ and H$_2$PO$_4^-$ were found to be too strong in acetonitrile to enable stability constants to be accurately determined.

¶ Analogous UV–VIS anion titration experiments with *meso*-tetraphenylporphyrin gave no evidence of Soret band perturbation.

‖ Electrochemical anion recognition experiments with *meso*-tetraphenylporphyrin gave no evidence of anion-induced redox couple perturbation.

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