Contribution from the Department of Chemistry,
University of Otago, P.O. Box 56, Dunedin, New Zealand

Acidity and Dimerization of Three Water-Soluble Iron(III) Porphyrin Cations: (*meso*-α,β,α,β-Tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrinato)iron(III), (*meso*-α,α,α,α-Tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrinato)iron(III), and (*meso*-Tetrakis(1-methylpyridinium-4-yl)porphyrinato)iron(III)[1,2]

Gordon M. Miskelly, Wayne S. Webley, Charles R. Clark, and David A. Buckingham*

Received December 9, 1987

The synthesis, or improved synthesis, of the parent porphyrin salts *meso*-α,α,α,α-tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrin triflate ($[\alpha_4\text{-(TMNP)H}_2](CF_3SO_3)_4$), *meso*-α,β,α,β-tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrin perchlorate ($[\alpha\beta\alpha\beta\text{-(TMNP)H}_2](ClO_4)_4$), and *meso*-tetrakis(1-methylpyridinium-4-yl)porphyrin triflate ($[(\text{TMPyP})H_2](CF_3SO_3)_4$) are described, as is the insertion of iron to form $[Fe(O_3SCF_3)(\alpha_4\text{-TMNP})](CF_3SO_3)_4$, $[FeBr(\alpha\beta\alpha\beta\text{-TMNP})Br_4$, $[FeBr(\text{TMPyP})](CdBr_4)_2$, and other salts. In aqueous solution at 25 °C the $[Fe(P)(OH_2)_2]^{5+}$ and $[Fe(P)(OH_2)(OH]^{4+}$ cations display the following $pK_{a1}{}^{m}$, $pK_{a2}{}^{m}$ values: 6.1, 10.28 ($P = \alpha\beta\alpha\beta$-TMNP, $I = 0.1$ mol dm^{-3}); 5.8, 10.0 ($P = \alpha_4$-TMNP, $I = 0.01$ mol dm^{-3}); 5.8, 11.7 (P = TMPyP, $I = 0.1$ mol dm^{-3}). Under the same conditions the $[Fe(P)(OH)(OH_2)]^{4+}$ cations dimerize to form μ-oxo-bridged species $\{Fe(P)\}_2O^{8+}$ with K_d values of $(1.8 \pm 0.7) \times 10^7$ dm^3 mol^{-1} ($P = \alpha_4$-TMNP), $(7.35 \pm 0.1) \times 10^3$ dm^3 mol^{-1} (P = TMPyP), and less than 1.2×10^3 dm^3 mol^{-1} ($P = \alpha\beta\alpha\beta$-TMNP, dimer not observed). Rate data for dimerization in the $P = \alpha_4$-TMNP, TMPyP systems have been obtained over the pH ranges 4.85–7.69 and 5.73–8.52, respectively, and have been interpreted in terms of dimerization of $[Fe(P)(OH_2)_2]^{5+}$ and $[Fe(P)(OH)(OH_2)]^{4+}$ units ($k_{f_2} = 1.2 \times 10^4$ mol^{-1} dm^3 s^{-1} (0.01 mol dm^{-3} NaNO$_3$) and 1.06×10^3 mol^{-1} dm^3 s^{-1} (0.1 mol dm^{-3} NaNO$_3$), respectively, at 25 °C). Hydrolysis of these dimers has been studied at pH 2.05–5.3 ($P = \alpha_4$-TMNP) and pH 1.38–10.48 and 0.01–0.50 mol dm^{-3} NaOH (P = TMPyP) and has been interpreted in terms of hydrolysis of $[\{Fe(P)\}_2(OH_2)]^{10+}$ ($k_{h_1}/K_{a_1}{}^{d} = 26.6$ mol^{-1} dm^3 s^{-1} (P = TMPyP)) and $[\{Fe(P)\}_2(OH)]^{9+}$ ($k_{h_2} \geq 40$ s^{-1} ($P = \alpha_4$-TMNP), 0.355 s^{-1} (P = TMPyP)) units under acidic conditions, and first order in [OH$^-$] hydrolysis of $[\{Fe(\text{TMPyP})\}_2O]^{8+}$ in alkali ($k_{h_3} = 2.9 \times 10^3$ mol^{-1} dm^3 s^{-1}, 0.1 mol dm^{-3} NaNO$_3$, 25 °C). Comparisons where appropriate are made with data recently reported by Tondreau and Wilkins.

Introduction

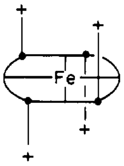
The recent pH–stopped-flow studies by El-Awady, Wilkins, and Wilkins[3] and Tondreau and Wilkins[4] on the dimerization and hydrolysis reactions of the water-soluble iron(III) porphyrins represented by (1) and (2)[2] prompts us to report our similar studies on the two cationic systems $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$ and $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$.

$$2[Fe(\text{TSPP})(OH_2)_2]^{3-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\text{TSPP})Fe\text{–}O\text{–}Fe(\text{TSPP})]^{8-} + 2H^+ + H_2O \quad (1)$$

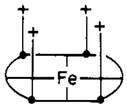
$$2[Fe(\text{TMPyP})(OH_2)_2]^{5+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [(\text{TMPyP})Fe\text{–}O\text{–}Fe(\text{TMPyP})]^{8+} + 2H^+ + H_2O \quad (2)$$

We also report our own observations on the $Fe(\text{TMPyP})^{5+}$ system since, although largely confirming those by Tondreau and Wilkins,[4] they were obtained under somewhat different electrolyte conditions and cover a wider pH range.

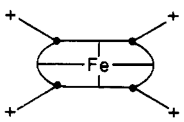
The three metalloporphyrins I–III form a graded series in which $Fe(\alpha\beta\alpha\beta\text{-TMNP})^{5+}$ has both sides of the porphyrin plane restricted toward further coordination and $Fe(\alpha_4\text{-TMNP})^{5+}$ has one face restricted, while $Fe(\text{TMPyP})^{5+}$ has both faces open toward coordination by a fifth and sixth ligand. The effect such restrictions have on the acidity of coordinated water molecules and on the rate and ability to dimerize are important issues in relation to the behavior of biologically important Fe(III) porphyrins.[5]



$Fe(\alpha\beta\alpha\beta\text{-TMNP})^{5+}$ (I)



$Fe(\alpha_4\text{-TMNP})^{5+}$ (II)



$Fe(\text{TMPyP})^{5+}$ (III)

Experimental Section

Preparations. Reagents were LR or AR grade where available, trifluoromethanesulfonic acid (Fluorad FC24, 3M Co.), *meso*-tetrakis(4-pyridyl)porphyrin (TPyPH_2, Strem Chemicals), and trimethyl phosphate (Koch-Light), with the last being dried over 4A sieves. Methyl trifluoromethanesulfonate was prepared by adding trifluoromethanesulfonic acid (100 cm^3, 1.13 mol) cautiously from a dropping funnel protected by a guard tube containing silica gel to freshly distilled (76 °C, 15 mmHg) dimethyl sulfate (100 cm^3, 1.06 mol). The methyl trifluoromethanesulfonate was then fractionally distilled (2 × 15 cm fractionation column) at 97 °C under anhydrous conditions to yield 107 g (97%) of a clear liquid, which was stored in a stoppered flask protected from light. (*Caution*! methyl trifluoromethanesulfonate is potentially *extremely hazardous*; inhalation of vapor and contact with skin should be avoided.[6]) Thin-layer chromatography on aluminum-backed Kieselgel 60F254 (Merck Art 5562) was used to monitor porphyrin syntheses and to check product purity.

Methylation of tetrapyridylporphine and insertion of iron has previously been reported by Fleischer and Hambright[7] and by Harris and Toppen,[8] and an IR assessment of the methylated complex has been given

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[1] Abstracted in part from: Webley, W. S. Ph.D. Thesis University of Otago, May 1984. Miskelly, G. M. Ph.D. Thesis, University of Otago, Oct 1986. The work described here formed the basis of a Conference Plenary Lecture, Royal Australian Chemical Institute (COMO-12), Hobart, Australia, Jan 1984.

[2] Abbreviations used for coordinated porphyrin dianions: TMPyP = tetrakis(1-methylpyridinium-4-yl)porphyrinato; TSPP = tetrakis(4-sulfonatophenyl)porphyrinato; TMNP = tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrinato; α_4 and $\alpha\beta\alpha\beta$ designate atropisomers; TTMPP = tetrakis(3,4,5-trimethylphenyl)porphyrinato; TCPP = tetrakis(4-carboxylatophenyl)porphyrinato; TMPP = tetrakis(4-methylphenyl)porphyrinato; TM_3PP = *meso*-tetrakis(2,4,6-trimethoxyphenyl)porphyrinato; TM_4PP = *meso*-tetramesitylporphyrinato; TSDMPP = tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrinato; DCMPIX = 2,4-dicysteinyl-*meso*-porphyrinato IX; PPIX = protoporphyrinato IX; DPIX = deuteroporphyrinato IX; DSDPIX = 2,4-disulfonatoprotoporphyrinato IX; TEnPPIX represents the tetraethylenediamine derivative of the protoporphyrinato IX dianion (see: Kolski, G. P.; Plane, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 3740); EDTA represents ethylenediaminetetraacetate.

[3] El-Awady, A. D.; Wilkins, P. C.; Wilkins, R. G. *Inorg. Chem.* **1985**, *24*, 2053.

[4] Tondreau, G. A.; Wilkins, R. G. *Inorg. Chem.* **1986**, *25*, 2745.

[5] Perutz, M. F.; Fermi, G.; Luisi, B.; Shaanan, B.; Liddington, R. C. *Acc. Chem. Res.* **1987**, *20*, 309.

[6] A fatal accident involving a small quantity of the related ester, methyl fluorosulfonate, is reported in: Van der Ham, D. M. W.; Van der Moor, D. *Chem. Eng. News* **1976**, *54(36)*, 5.

[7] Fleischer, E. B.; Hambright, F. *Inorg. Chem.* **1970**, *9*, 1759.

[8] Harris, F. L.; Toppen, D. L. *Inorg. Chem.* **1978**, *17*, 71.

0020-1669/88/1327-3773$01.50/0

by Forshey and Kuwana.[9] The following synthetic method has been found to be more satisfactory and avoids the hazards of potentially explosive perchlorate salts.

***meso*-Tetrakis(1-methylpyridinium-4-yl)porphyrin Trifluoromethanesulfonate, $[(TMPyP)H_2](CF_3SO_3)_4$.** $(TPyP)H_2$ (1.0 g) was suspended in dry trimethyl phosphate (15 cm^3) containing 2,6-lutidine (0.25 g). Methyl trifluoromethanesulfonate (2.0 g) was added and the mixture stirred in a stoppered flask for 5 min. Further 2,6-lutidine (0.15 g) was then added to the now green-brown solution, and this mixture was stirred for 1.5 h before being poured into water (300 cm^3). The aqueous mixture was cooled at 0 °C for 30 min, and the resulting purple crystalline solid was removed and washed with water (2 × 100 cm^3), 2-propanol (2 × 30 cm^3), and ether (50 cm^3) and air-dried (yield 1.90 g, 93%). This product was recrystallized from hot methanol (450 cm^3) by adding hot (60 °C) 2-propanol (600 cm^3) and cooling in ice. The crystalline purple product (1.74 g, 85%) was filtered off, washed with 2-propanol and ether, and dried in air. Anal. Calcd for $C_{48}H_{38}N_8O_{12}F_{12}S_4$: C, 45.2; H, 3.00; N, 8.79; F, 17.9; S, 10.0. Found: C, 45.4; H, 3.35; N, 8.85; F, 17.9; S, 10.2. Electronic spectrum (ϵ, 10^4 mol^{-1} dm^3 cm^{-1} (λ, nm); MeOH): 25 (424), 1.8 (514), 0.63 (590), 0.14 (647). ^1H NMR (90 MHz, Me_2SO-d_6): δ 9.8 (d, 8 H, pyridyl CH), 9.47 (s, 8 H, pyrrole CH), 9.30 (d, 8 H, pyridyl CH), 4.93 (s, 12 H, methyl CH), −2.90 (s, 2 H, pyrrole NH). TLC: R_f 0.17 (H_2O:HOAc:py:MeOH, 2:2:1:1).

***meso*-$\alpha,\alpha,\alpha,\alpha$-Tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrin Trifluoromethanesulfonate, $[\alpha_4\text{-}(TMNP)H_2](CF_3SO_3)_4$.** To a stirred suspension of $\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-nicotinamidophenyl)porphyrin[10] (α_4-$(TNP)H_2$, 2.0 g) in dry trimethyl phosphate (20 cm^3) was added methyl trifluoromethanesulfonate (2.5 g). After 30 min the green solution was poured into water (400 cm^3) and the resultant purple precipitate filtered off, washed with water (3 × 50 cm^3), and dried under vacuum. The porphyrin was crystallized from methanol (300 cm^3) following addition of 2-propanol and slow reduction of the solution volume (rotary evaporator, 25 °C) to 100 cm^3. The crystalline product (2.4 g, 75%) was filtered off, washed with 2-propanol, and air-dried. Anal. Calcd for $C_{76}H_{58}N_{12}O_{16}F_{12}S_4$: C, 52.1; H, 3.3; N, 9.6; F, 13.0; S, 7.3. Found: C, 52.4; H, 3.4; N, 9.4; F, 13.1; S, 7.6. ^1H NMR (90 MHz, Me_2SO-d_6): δ 10.97 (s, 4 H, amide NH), 8.98 (s, 8 H, pyrrole CH), 8.85–7.53 (m, 32 H, phenyl and pyridyl CH), 4.13 (s, 12 H, CH_3), −2.88 (s, 2 H, pyrrole NH). TLC: R_f 0.20 (H_2O:HOAc:py:MeOH, 2:2:1:1).

***meso*-$\alpha,\beta,\alpha,\beta$-Tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrin Perchlorate, $[\alpha\beta\alpha\beta\text{-}(TMNP)H_2](ClO_4)_4$.** To a stirred solution of the mixed atropisomers of tetrakis(*o*-nicotinamidophenyl)porphyrin[10] ($(TNP)H_2$, 2.86 g) in dry trimethyl phosphate (30 cm^3) was added methyl trifluoromethanesulfonate (3 cm^3) and 2,6-lutidine (2 cm^3). After 30 min further methyl trifluoromethanesulfonate (1 cm^3) and 2,6-lutidine (0.5 cm^3) were added and the solution was stirred for another 45 min before the reaction was quenched by addition of methanol (20 cm^3). The resultant solution was slowly poured into rapidly stirred ether (500 cm^3) and the precipitated product isolated by filtration on Celite. It was washed from the filter cake with methanol and reprecipitated by addition of 2-propanol and ether. The isolated solid was dissolved in HCl (800 cm^3, 0.75 mol dm^{-3}) and the filtered green solution degassed (nitrogen bubbling) and irradiated with visible light[11] (500-W tungsten lamp, 200-W Hg lamp equipped with soda-glass filter) in a flask fitted with a cold-finger condenser, stirrer, and nitrogen inlet. After 10 h TLC (H_2O:HOAc:py:MeOH, 2:2:1:1) showed that >90% of the tetrakis(*o*-nicotinamidophenyl)porphyrin was in the $\alpha,\beta,\alpha,\beta$ conformation. The solution was stirred and $NaClO_4$ added until a green precipitate began to form. The suspension was made alkaline (NH_4OH), and the precipitated porphyrin was filtered off, washed thoroughly with water, then with 2-propanol, and finally with ether. The resulting hygroscopic purple solid was taken up in water (1 dm^3) containing NH_4OH sp gr 0.91, 10 cm^3) and the solution sorbed onto Sephadex SP-C25 ion-exchange resin (30 × 7 cm). The column was washed with NH_4OH (2 mol dm^{-3}) and the porphyrin removed by gradient elution (2 mol dm^{-3} NH_4OH and NaCl (0.3 mol dm^{-3}) containing 2 mol dm^{-3} NH_4OH). The product was isolated following adjustment to pH 7 ($HClO_4$) and addition of excess $NaClO_4$. Recrystallization was effected by slow evaporation (rotary evaporator) of a methanol–acetone–2-propanol solution. Anal. Calcd for $C_{72}H_{58}N_{12}O_{20}$: C, 55.7; H, 3.8; N, 10.8. Found: C, 53.6; H, 3.6; N, 10.8. Electronic spectrum (ϵ, 10^4 mol^{-1} dm^3 cm^{-1} (λ, nm); MeOH): 32.6 (422), 1.63 (517), 0.49 (551), 0.52 (592), 0.18 (647). TLC: R_f 0.40 (H_2O:HOAc:py:MeOH, 2:2:1:1).

Bromo(*meso*-tetrakis(1-methylpyridinium-4-yl)porphyrinato)iron(III) Salts. Method a. To $[(TMPyP)H_2](CF_3SO_3)_4$ (200 mg) in pyridine (5 cm^3) and acetic acid (10 cm^3) was added aqueous $FeSO_4$ (0.3 cm^3, saturated solution). The resulting solution was maintained at 90 °C under nitrogen for 30 min. The solvent was removed (rotary evaporator, 90 °C, 4 h) and the residue redissolved in HBr (0.1 mol dm^{-3}, 15 cm^3), and this solution filtered. Adding aqueous LiBr (saturated solution) to the filtrate at 60 °C and subsequent slow cooling resulted in the formation of purple-black crystals, which were removed and washed with 2-propanol and air-dried. The purple crystalline solid (137 mg, 89%) was recovered after recrystallization from hot methanol–2-propanol solution. Anal. Calcd for $[Fe(TMPyP)](CF_3SO_3)_{0.4}Br_{3.6}\cdot 6H_2O$: C, 42.0; H, 3.97; N, 8.83; Br, 28.9; S, 1.01. Found: C, 40.8; H, 3.69; N, 8.71; Br, 30.7; S, 0.58. Electronic spectrum (ϵ, 10^3 mol^{-1} dm^3 cm^{-1} (λ, nm); 0.1 mol dm^{-3} HNO_3): 95.3 (400), 8.78 (480), 10.3 (520), 7.99 (536), 3.85 (560), 3.15 (580), 2.92 (595), 3.41 (630) (cf. $\epsilon_{400} = 10^5$ mol^{-1} dm^3 cm^{-1}).[5] TLC: R_f 0.12 (H_2O:HOAc:py:MeOH, 2:2:1:1).

Method b. Cd^{2+}-Catalyzed Iron Insertion. To $[(TMPyP)H_2](CF_3SO_3)_4$ (103 mg) in methanol–water (1:1, 20 cm^3) containing pyridine (0.2 cm^3) was added $Cd(NO_3)_2\cdot 4H_2O$ (86 mg). The solution changed from red-purple to green (3 min) and was deoxygenated (15 min of Ar bubbling), following which $FeCl_2\cdot 4H_2O$ (131 mg) was added. Stirring for 3 h under Ar resulted in a red solution. This was acidified (red to yellow color change) and diluted to 75 cm^3 with water and the porphyrin precipitated by addition of LiBr (1 cm^3, saturated solution). The precipitate was collected on a Whatman GFC filter and washed with 2-propanol. The porphyrin in boiling water (50 cm^3) was crystallized by addition of LiBr (1.5 cm^3, saturated solution) followed by slow cooling to 0 °C. Purple crystals (59 mg) were filtered off, washed with 2-propanol and ether, and dried in air. Anal. Calcd for $[FeBr(TMPyP)](CdBr_4)_2$: C, 32.5; H, 2.28; N, 6.68; Cd, 13.4; Br, 42.8. Found: C, 31.9; H, 2.60; N, 6.35; Cd, 12.8; Br, 42.7. Analysis also indicated the presence of some S (0.70%). This could not be explained by the presence of $CF_3SO_3^-$ as the appropriate IR bands were absent. The cadmium was removed as follows. To $[FeBr(TMPyP)](CdBr_4)_2$ (250 mg) in water (150 cm^3) was added NaOH solution (2 cm^3, 5 mol dm^{-3}). The resulting white precipitate was removed on a Whatman GFC filter paper, and aqueous LiBr (4 cm^3, saturated solution) was added to the filtrate. This was then acidified with HBr (48%), reduced in volume to 25 cm^3, and cooled on ice. The resulting purple crystals (125 mg) were collected, washed with 2-propanol, and air-dried. Anal. Found: Cd, <0.02.

(Trifluoromethanesulfonato)(*meso*-$\alpha,\alpha,\alpha,\alpha$-tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrinato)iron(III) Trifluoromethanesulfonate, $[Fe(O_3SCF_3)(\alpha_4\text{-}TMNP)](CF_3SO_3)_4$. To a stirred solution of $[\alpha_4\text{-}(TMNP)H_2](CF_3SO_3)_4$ (2.5 g) in acetic acid (100 cm^3) and pyridine (2 cm^3) was added $FeSO_4$ (2 cm^3, saturated solution) and the mixture heated at 50 °C for 30 min. The solvent was removed by rotary evaporation and the dry residue taken up in warm methanol (250 cm^3). Sodium trifluoromethanesulfonate (15 g) was added to the filtered solution and the volume slowly reduced (rotary evaporator) to ~60 cm^3. The resulting purple-black crystalline product was filtered off, washed with 2-propanol, and recrystallized from methanol–2-propanol solution (yield 2.4 g, 87%). Anal. Calcd for $C_{77}H_{56}N_{12}O_{19}F_{15}S_5Fe$: C, 47.3; H, 2.9; N, 8.6; S, 8.2. Found: C, 47.5; H, 3.4; N, 9.0; S, 7.6. Electronic spectrum: (ϵ, 10^4 mol^{-1} dm^3 cm^{-1} (λ, nm); 0.01 mol dm^{-3} HNO_3): 1.11 (528), 0.30 (570, sh), 0.25 (650, sh), 0.26 (670). TLC: R_f 0.12 (H_2O:HOAc:py:MeOH = 2:2:1:1).

Bromo(*meso*-$\alpha,\beta,\alpha,\beta$-tetrakis(*o*-(*N*-methylnicotinamido)phenyl)porphyrinato)iron(III) Bromide, $[FeBr(\alpha\beta\alpha\beta\text{-}TMNP)]Br_4$. Solid $Cd(NO_3)_2\cdot 4H_2O$ (2.2 g) was added to a solution of $[\alpha\beta\alpha\beta\text{-}(TMNP)H_2](ClO_4)_4$ (2.2 g) and pyridine (4 g) in water–methanol (1:1, 400 cm^3) under an argon atmosphere. After 20 min $FeSO_4\cdot 7H_2O$ (2.7 g) was added to the green solution, which was stirred under argon for 4 h. Addition of HBr (48%, 5 cm^3) precipitated the product, which was filtered off, washed with 2-propanol and then ether, and air-dried. A filtered solution of the porphyrin in water–methanol (1:1, 600 cm^3, 40 °C) was then reprecipitated by using concentrated HBr (4 cm^3), LiBr (2 g), and $Cd(NO_3)_2\cdot 4H_2O$ (0.5 g). The resultant solid was dissolved in aqueous NaOH (0.2 mol dm^{-3}, 220 cm^3), the solution was filtered, and HBr (14 cm^3) and LiBr (2 g) were added. Following reduction of the solution volume (to ~120 cm^3) and cooling the product was filtered off, dried, and crystallized by slow evaporation (rotary evaporator) of a methanol–2-propanol solution (yield 1.40 g, 61%). Anal. Calcd for $C_{72}H_{56}N_{12}O_4FeBr_5$: C, 53.8; H, 3.5; N, 10.5; Br, 24.8. Found after drying to constant mass at 100 °C and 0.1 mmHg: C, 53.5; H, 3.9; N, 9.6; Br, 25.6. The weight loss on drying corresponded to 5 H_2O per Fe. Electronic spectrum (ϵ, 10^4 mol^{-1} dm^3 cm^{-1} (λ, nm); 0.10 mol dm^{-3} HCl): 10.3 (401), 1.07 (531), 0.22 (672). TLC: R_f 0.32 (H_2O:HOAc:py:MeOH, 1:2:2:1).

Equilibrium Measurements. Visible absorption spectra were recorded on a Cary 219 spectrophotometer. pH measurements were made with

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(9) Forshey, P. A.; Kuwana, T. *Inorg. Chem.* **1983**, *22*, 699.

(10) Buckingham, D. A.; Gunter, M. J.; Mander, L. N. *J. Am. Chem. Soc.* **1978**, *100*, 2899.

(11) Freitag, R. A.; Whitten, D. G. *J. Phys. Chem.* **1983**, *87*, 3918.

a Radiometer pHM62 pH meter equipped with G202B glass and K4040 saturated calomel electrodes. The system was calibrated with NBS specification buffers.[12] Electrolytes were generally of AR quality. MES (Calbiochem), CAPS (Sigma), and HEPES, TRIS, and PIPES (Ultrol, Calbiochem), were used without further purification. Solutions of the iron(III) porphyrins were standardized spectrophotometrically by using the extinction coefficients given in Preparations. Simultaneous pH and spectral measurements were made by using a flow-through 1 cm path length cuvette connected via a peristaltic pump to a Radiometer pH/titration assembly. Because $Fe(TMPyP)^{5+}$ (in particular) is adsorbed by glass and quartz at high pH, the connecting tubing used was either PVC or Tygon, and plastic titration and spectrophotometer cells were used for measurements under these conditions.

pK_{a_1} Measurements. A 40-cm^3 portion of a solution containing either $[Fe(TMPyP)(OH_2)_2]^{5+}$ (2.68×10^{-6} mol dm^{-3}) or $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$ (5.7×10^{-6}–4.5×10^{-5} mol dm^{-3}), the required amount of $NaNO_3$ as supporting electrolyte, and MES (acid form, 0.005–0.01 mol dm^{-3}) was cycled (15 cm^3 min^{-1}) through a flow-through cell. pH adjustments were made by the addition of small volumes (25–200 μL) of HNO_3 (2–4 mol dm^{-3}) or NaOH (1–4 mol dm^{-3}) and the solution circulated until both absorbance and pH readings had stabilized. Absorbance values (±0.0005) were then noted from the spectrophotometer digital display (400 nm, $[Fe(TMPyP)(OH_2)_2]^{5+}$; 400, 480, 530, or 630 nm, $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$). Some measurements were also made at 400 nm with use of a hand-operated rapid-mixing device to mix a solution of $[Fe(TMPyP)(OH_2)_2]^{5+}$ (2.60×10^{-5} mol dm^{-3}) and $NaNO_3$ (0.1 mol dm^{-3}) containing MES (acid form, 0.01 mol dm^{-3}) with a solution of $NaNO_3$ (0.1 mol dm^{-3}) that contained sufficient NaOH to give the desired final pH. pH measurements were made on the effluent solution. The stopped-flow spectrophotometer was used to determine pK_{a_1} for $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$. An iron(III) porphyrin solution (3.05×10^{-5} mol dm^{-3}, pH 3.0, $I = 0.01$ mol dm^{-3} ($NaNO_3$)) was rapidly mixed with a series of MES buffers ((3–6) $\times 10^{-3}$ mol dm^{-3}) adjusted to $I = 0.01$ mol dm^{-3} ($NaNO_3$). Absorbance readings (528 nm) were taken within 10 ms of mixing over the pH range 4.95–6.54, and the limiting absorbance of $[Fe(\alpha_4\text{-TMNP})(OH_2)(OH)]^{4+}$ was obtained by using HEPES buffer (pH 7.91) in place of MES.

pK_{a_2} Measurements. A 40-cm^3 portion of a solution containing $[Fe(TMPyP)(OH_2)_2]^{5+}$ (1.74×10^{-4} mol dm^{-3}), Na_2CO_3 (0.01 mol dm^{-3}), and NaOH (0.1 mol dm^{-3}) or $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$ (4×10^{-5} mol dm^{-3}), CAPS (0.1 mol dm^{-3}), and NaOH (0.01 or 0.10 mol dm^{-3}), adjusted to the desired ionic strength ($NaNO_3$), was cycled through the flow-through cell as described above. pH adjustments were made by the addition of small volumes of HNO_3 (70%, or 2 mol dm^{-3}), and the solution absorbance was recorded at 594 and 633 nm ($[Fe(TMPyP)(OH_2)_2]^{5+}$) or 670 nm ($[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$). A solution of $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$ (6.3×10^{-6} mol dm^{-3}, pH 3.0) was pH-jumped to either pH 8.2 (TRIS, 0.002 mol dm^{-3}) or to a final $[OH^-]$ of 0.01 mol dm^{-3} by using the hand-operated mixing device described above, and spectra in the Soret region were recorded within 50 s. A spectrum intermediate between those for the limiting forms $[Fe(\alpha_4\text{-TMNP})(OH)_2]^{3+}$ (λ_{max} 422 nm, ϵ 1.05×10^5 mol^{-1} dm^3 cm^{-1}) and $[Fe(\alpha_4\text{-TMNP})(OH_2)(OH)]^{4+}$ (λ_{max} 417 nm, ϵ 1.08×10^5 mol^{-1} dm^3 cm^{-1}) was recorded when the solution pH was jumped to 10.0 (0.001 mol dm^{-3} CAPS, $I = 0.01$ mol dm^{-3} ($NaNO_3$), 25.0 °C).

K_d Measurements. A stock solution of $[Fe(TMPyP)(OH_2)_2]^{5+}$ (8.75×10^{-3} mol dm^{-3}) containing $NaNO_3$ (0.1 mol dm^{-3}) and HEPES (0.01 mol dm^{-3}) was adjusted to pH 7.45 with NaOH (1 mol dm^{-3}). Aliquots were diluted to the desired concentration with a buffer solution of $NaNO_3$ (0.1 mol dm^{-3}) and HEPES (0.01 mol dm^{-3}), pH 7.45, previously filtered through a Whatman GFC glass-fiber filter. Spectral scans showed isosbestic points at 560 and 580 nm, and measurements at these wavelengths were used to check that dilutions had been carried out correctly and that no porphyrin had been lost through adsorption. A 0.1 cm path length quartz cuvette was used at high porphyrin concentrations and a 1-cm plastic cell at lower concentrations. The base line was prerecorded with use of the buffer solution and checked at the end of each set of measurements. Spectra were recorded until equilibrium was reached, and final adsorbance readings (±0.0005) were taken from the digital display.

A solution of $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$ (40 cm^3, 8.13×10^{-5} mol dm^{-3}) 0.001 mol dm^{-3} in HEPES and $I = 0.01$ mol dm^{-3} ($NaNO_3$) was adjusted to pH 6.0. After dimer formation was complete (~1 h), the solution was cycled through the flow-through cell and the pH adjusted (0.1–1.0 mol dm^{-3} HNO_3) in steps of ~0.2 pH unit to pH 3.0. Following each adjustment the solution was circulated until relaxation was complete and the pH had stabilized (5–15 min); the solution spectrum (700–440 nm) was then recorded.

Table I. Spectrophotometric pK_a Values[a] for Monomeric Iron(III) Porphyrins at 25 °C

compd	I,[b] mol dm^{-3}	$pK_{a_1}{}^m$	$pK_{a_2}{}^m$
$[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$	0.050	5.88 ± 0.04	...
	0.10	6.09 ± 0.09[d]	10.28
	0.25	6.40 ± 0.04	...
	0.50	6.59 ± 0.04	10.43
	1.0	6.72 ± 0.04[e]	...
$[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$	0.010	5.79 ± 0.06	10.0 ± 0.2
$[Fe(TMPyP)(OH_2)_2]^{5+}$	0.10	5.79 ± 0.08[c]	11.71 ± 0.05

[a] pK_a values are mixed constants incorporating concentrations of iron porphyrin species and hydrogen ion activity. [b] Ionic strength maintained with $NaNO_3$. [c] At $[Fe(P)]_T = 2.68 \times 10^{-6}$ mol dm^{-3} and $\lambda = 400$ nm. An additional determination with $[Fe(P)]_T = 7.35 \times 10^{-6}$ mol dm^{-3} and $\lambda = 450$ nm gave an identical result. [d] Mean value from six determinations. [e] A value of 6.88 ± 0.04 was obtained with NaCl as supporting electrolyte.

Kinetic Measurements. Kinetic experiments were carried out by using either a Cary 219 spectrophotometer, equipped with a rapid-mixing device when required, or a Durrum D-110 stopped-flow spectrophotometer linked to a Biomation waveform recorder, Tektronix oscilloscope, and Varian recorder. For some experiments a Harrick rapid-scan monochromator incorporating an OLIS data collection system was used in conjunction with the Durrum. Rate data were obtained by using the pH-jump–concentration-jump technique.

Monomer–Dimer Interconversion. For reactions of $Fe(TMPyP)^{5+}$ in the pH range 6–10.5 an iron porphyrin solution (5–100 μL, 2.24×10^{-3} or 3.54×10^{-3} mol dm^{-3}, pH 7.5, $I = 0.1$ mol dm^{-3} ($NaNO_3$)) was injected into 3.0 cm^3 of buffer solution ($I = 0.1$ mol dm^{-3} ($NaNO_3$)) contained in a 1-cm cell. The first-order data were collected at 520 nm over about 3 half-lives. For pH <6 the observed rate constants were independent of iron porphyrin concentration and the reactions were monitored (520 nm) following rapid mixing (stopped flow) of equal volumes of iron porphyrin solution (14.3×10^{-5} or 7.15×10^{-5} mol dm^{-3}, pH ~8 (NaOH), $I = 0.1$ mol dm^{-3} ($NaNO_3$)) and buffer or HNO_3 solution ($I = 0.1$ mol dm^{-3} ($NaNO_3$)). In all cases effluents from duplicate runs were combined for subsequent pH measurement.

Formation of the dimer in the $Fe(\alpha_4\text{-TMNP})^{5+}$ system was monitored at 569 nm following rapid mixing of equal volumes of monomer solution ((13.1–8.94) $\times 10^{-5}$ mol dm^{-3}, pH 3.0, $I = 0.01$ mol dm^{-3} ($NaNO_3$)) and buffer (MES, HEPES, PIPES, or TRIS, 3.5×10^{-3} mol dm^{-3}, $I = 0.01$ mol dm^{-3} ($NaNO_3$)). Concentrations of monomer species at equilibrium were calculated by using the previously determined values of $pK_{a_1}{}^m$ and K_d (5.8 and 1.8×10^7 mol^{-1} dm^3, respectively) and rate constants obtained from linear plots of $1/([M]_t - [M]_e)$ versus time, where $[M]_t$ and $[M]_e$ represent the concentrations of monomer species at time t and at equilibrium, respectively. For reaction of the dimer at pHs below 4 solutions of $Fe(\alpha_4\text{-TMNP})^{5+}$ (6.84×10^{-5} mol dm^{-3}, pH 7.0, $I = 0.01$ mol dm^{-3} ($NaNO_3$)) were mixed with equal volumes of HNO_3 or HEPES buffer and the decrease in absorbance was monitored at 528 nm. For reaction of the dimer at pHs above 4 15–100 μL of iron porphyrin solution (3.7×10^{-4} mol dm^{-3}, pH 7) was added to 2.5 cm^3 of buffer solution (pyridine (2–4) $\times 10^{-3}$ mol dm^{-3}, $I = 0.01$ mol dm^{-3} ($NaNO_3$)) and the absorbance change monitored at 387 nm. First-order traces were obtained in all cases.

Results

Proton Equilibria. $pK_a{}^m$ data (25 °C) for the monomeric iron(III) porphyrins (eq 3 and 4) were determined by spectrophotometric titration and are listed in Table I. Conventional

$$[Fe(P)(OH_2)_2]^{5+} + H_2O \xrightleftharpoons{K_{a_1}{}^m} [Fe(P)(OH_2)(OH)]^{4+} + H_3O^+ \tag{3}$$

$$[Fe(P)(OH_2)(OH)]^{4+} + H_2O \xrightleftharpoons{K_{a_2}{}^m} [Fe(P)(OH)_2]^{3+} + H_3O^+ \tag{4}$$

titrations were possible for $P = \alpha\beta\alpha\beta$-TMNP since this system remains monomeric over the full pH range 2–12. All species were soluble up to ionic strength 1.0 mol dm^{-3}, and the results show a strong medium effect, particularly for pK_{a_1}. Figure 1I shows limiting spectra for $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$, $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)(OH)]^{4+}$, and $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH)_2]^{3+}$.

For the $P = \alpha_4$-TMNP system there is a marked tendency to dimerize (see below); the determination of $pK_{a_1}{}^m$ required rapid pH adjustment from 3.0 to 5–7.9, and spectral measurement before

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(12) Linnett, N. *pH Measurements in Theory and Practice*; Radiometer: Copenhagen, 1970; p 157.

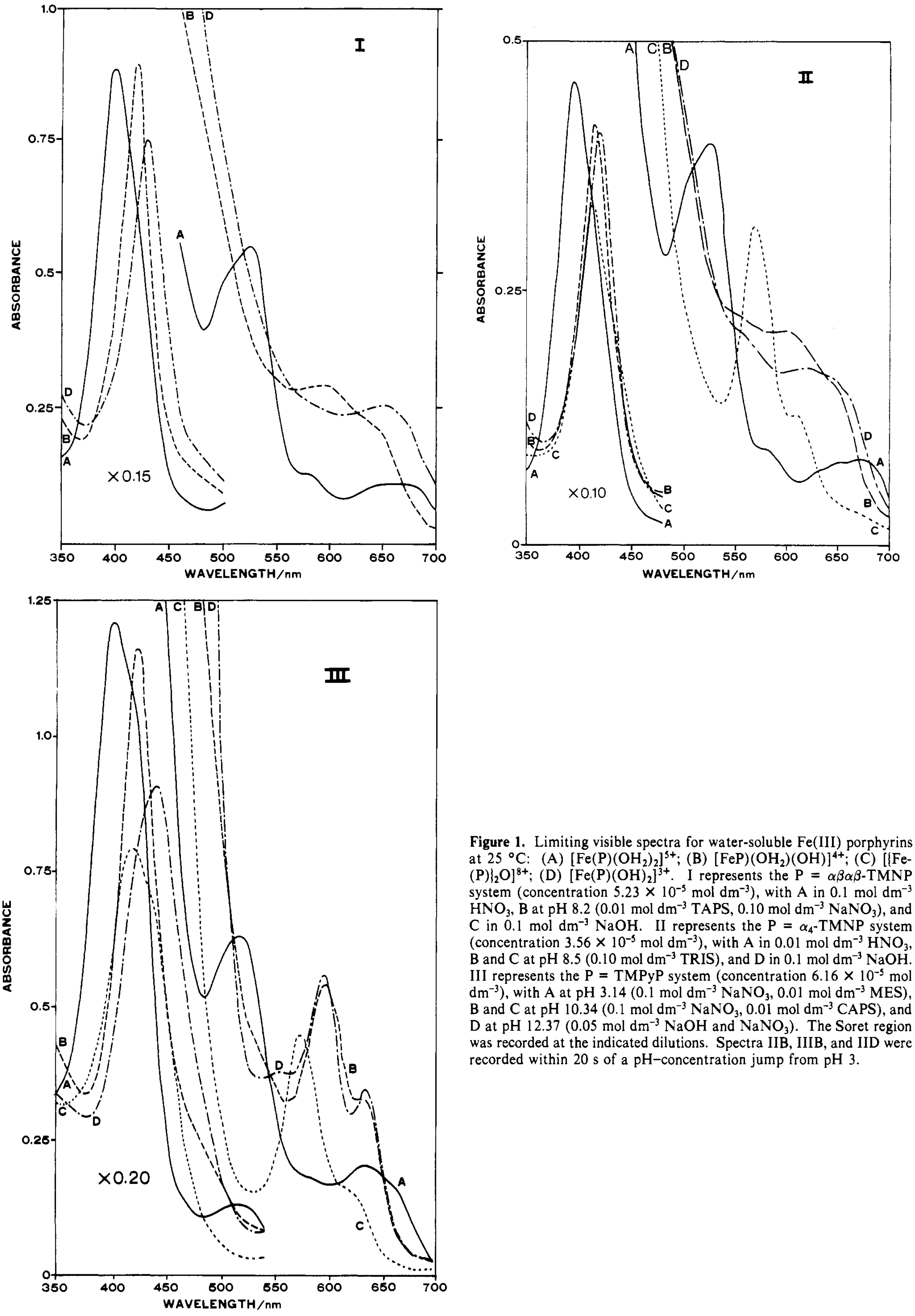

Figure 1. Limiting visible spectra for water-soluble Fe(III) porphyrins at 25 °C: (A) $[Fe(P)(OH_2)_2]^{5+}$; (B) $[FeP)(OH_2)(OH)]^{4+}$; (C) $[\{Fe(P)\}_2O]^{8+}$; (D) $[Fe(P)(OH)_2]^{3+}$. I represents the P = $\alpha\beta\alpha\beta$-TMNP system (concentration 5.23×10^{-5} mol dm^{-3}), with A in 0.1 mol dm^{-3} HNO_3, B at pH 8.2 (0.01 mol dm^{-3} TAPS, 0.10 mol dm^{-3} $NaNO_3$), and C in 0.1 mol dm^{-3} NaOH. II represents the P = α_4-TMNP system (concentration 3.56×10^{-5} mol dm^{-3}), with A in 0.01 mol dm^{-3} HNO_3, B and C at pH 8.5 (0.10 mol dm^{-3} TRIS), and D in 0.1 mol dm^{-3} NaOH. III represents the P = TMPyP system (concentration 6.16×10^{-5} mol dm^{-3}), with A at pH 3.14 (0.1 mol dm^{-3} $NaNO_3$, 0.01 mol dm^{-3} MES), B and C at pH 10.34 (0.1 mol dm^{-3} $NaNO_3$, 0.01 mol dm^{-3} CAPS), and D at pH 12.37 (0.05 mol dm^{-3} NaOH and $NaNO_3$). The Soret region was recorded at the indicated dilutions. Spectra IIB, IIIB, and IID were recorded within 20 s of a pH–concentration jump from pH 3.

relaxation to the dimer was appreciable (<10 ms). The low solubility of the resulting aqua–hydroxo monomer in solutions of noncoordinating anions (NO_3^-, ClO_4^-, $CF_3SO_3^-$, PF_6^-) restricted the ionic strength to 0.01 mol dm^{-3}. The small spectral change associated with subsequent ionization of $[Fe(\alpha_4\text{-TMNP})(OH_2)(OH)]^{4+}$ (cf. Figure 1II together with its relatively rapid dimerization at pHs in the region of pK_{a_1} prevented an accurate measure of $pK_{a_2}{}^{m}$. The value of 10.0 ± 0.2 (Table I) is assigned on the basis that when a solution of the diaqua complex (6.3×10^{-6} mol dm^{-3}, pH 3.0) was adjusted to pH 10.0 the initial spectrum (rapid scan) observed in the Soret region (350–450 nm) was exactly intermediate between those recorded for the aqua–hydroxo (at pH 8.2) and dihydroxo (at pH 12.0) complexes.

For P = TMPyP in the pH range 4.3–7.5 at concentrations less than 7×10^{-6} mol dm^{-3} ($I = 0.1$ mol dm^{-3}, $NaNO_3$) less than 2% of the complex is present as the μ-oxo dimer at equilibrium. Under such conditions the spectrophotometric data could be analyzed as a single acid–base process ($pK_{a_1}{}^{m} = 5.79$, Table I). When more concentrated solutions were used, the increasing presence of dimer did not result in the loss of isosbestic points, although calculated $K_{a_1}{}^{m}$ values showed increasing variation. At the high pHs necessary to obtain $pK_{a_2}{}^{m}$, formation of the dimer is very slow ($[Fe(TMPyP)]_T = 1.74 \times 10^{-4}$ mol dm^{-3}) and could be ignored over the times required for proton equilibration and measurement. However, the use of a plastic flow-through cell was necessary to avoid surface adsorption effects found with glass and silica. This is the likely cause of the difficulty experienced by Kurihara et al.[13] in maintaining a constant spectrum in strong alkali. A limiting spectrum for $[Fe(TMPyP)(OH)_2]^{3+}$ was not obtainable at $I = 0.1$ mol dm^{-3}, and the graphical method of Albert and Serjeant[14] was used to evaluate $pK_{a_2}{}^{m}$. Figure 1III gives the observed spectra for species in this system.

Dimerization Equilibria. The absorption spectrum of $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)(OH)]^{4+}$ at pH 7.45, particularly in the region 570–650 nm, shows no change with time over the concentration range 1×10^{-5}–5×10^{-3} mol dm^{-3} ($I = 0.1$ mol dm^{-3} ($NaNO_3$)). This wavelength range should maximize detection of the μ-oxo dimer (Figure 1II,III), and assuming that a 10% depletion in aqua–hydroxo monomer would have been detected at 5×10^{-3} mol dm^{-3} (based on the data for $Fe(\alpha_4\text{-TMNP})^{5+}$), this gives $K_d < (0.25 \times 10^{-3})/(4.5 \times 10^{-3})^2$, or less than 1.2×10^2 dm^3 mol^{-1}. Thus, $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)(OH)]^{4+}$ remains monomeric in water at all useful concentrations.

For $Fe(\alpha_4\text{-TMNP})^{5+}$ the dimerization constant

$$K_d = \frac{[[\{Fe(P)\}_2O]^{8+}]}{[[Fe(P)(OH_2)(OH)]^{4+}]^2} \tag{5}$$

was obtained by spectrophotometric titration of a 8.13×10^{-5} mol dm^{-3} solution from pH 6 to pH 3 ($I = 0.01$ mol dm^{-3} ($NaNO_3$)). Figure 2 shows such a titration with each spectrum representing the equilibrium condition. Isosbestic points are maintained at 483, 551, and 619 nm, and the concentration of aqua–hydroxo monomer never exceeds 2% of the total porphyrin at any pH. Limiting spectra represent $(Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$ (λ_{max} 528 nm) and $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ (λ_{max} 569 nm). Absorbance data (528 nm) over the pH range 5.01–3.59 were analyzed according to eq 7, giving $K^1{}_d = (4.7 \pm 0.4) \times 10^{-5}$ mol dm^{-3}, whence K_d (eq 5)

$$2[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+} \xrightleftharpoons{K^1{}_d} [\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+} + 2H^+ + 3H_2O \tag{6}$$

$$K^1{}_d = \frac{[[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}]a_{H^+}{}^2}{[[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}]^2} \tag{7}$$

$= K^1{}_d/K_{a_1}{}^2 = (1.8 \pm 0.7) \times 10^7$ dm^3 mol^{-1}. It is important to note that good agreement was obtained for all the data, including that at lowest pH, which implies a two-proton change on forming the dimer under these conditions.

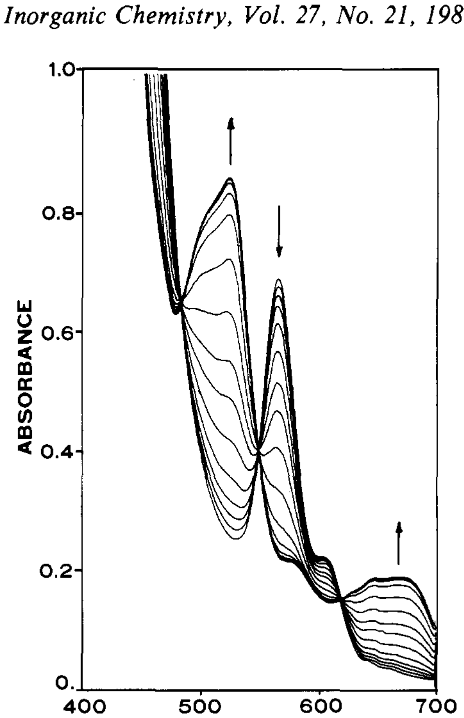

Figure 2. Spectral changes accompanying pH titration of the dimer $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ ($[Fe]_T = 8.13 \times 10^{-5}$ mol dm^{-3}, $I = 0.01$ mol dm^{-3} ($NaNO_3$), 25 °C) to give $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$. Spectra were recorded at pH 6.00 (initial), 5.49, 5.22, 5.01, 4.79, 4.56, 4.36, 4.22, 4.04, 3.83, 3.59, 3.38, 3.18, and 3.00.

For the P = TMPyP system experiments using long- or short-path-length cells showed that limiting spectra could not be obtained for the pure monomeric $[Fe(TMPyP)(OH_2)(OH)]^{4+}$ or dimeric $[\{Fe(TMPyP)\}_2O]^{8+}$ species. Surface adsorption effects plagued the former measurement, and the latter required a too optically dense solution. Absorbance data at equilibrium for serial dilutions from 8.75×10^{-3} to 3.5×10^{-6} mol dm^{-3} at pH 7.45 were therefore fitted to eq 5 by using a nonlinear least-squares regression program[15] that optimized K_d and the extinctions of the monomer and dimer at 520, 536, and 597 nm. Isosbestic points for such mixtures occurred at 560 and 580 nm (cf. Tondreau and Wilkins[4]), and extinction coefficients at these wavelengths were used to check that there was no loss of porphyrin through adsorption. Analysis gave $K_d = (7.35 \pm 0.10) \times 10^3$ dm^3 mol^{-1} ($I = 0.1$ mol dm^{-3} ($NaNO_3$)) (cf. Tondreau and Wilkins,[4] 2×10^3 dm^3 mol^{-1}, $I = 0.005$ mol dm^{-3} in buffer).

Dimerization and Hydrolysis Kinetics. Hydrolysis of $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ was studied spectrophotometrically by using the combined pH-jump–concentration-jump–stopped-flow method. A solution of dimer at pH 7 was jumped to a pH in the range 2.0–5.3. The spectrum changed with time either to that of the monomer or to that of a new equilibrium mixture of monomer and dimer. First-order rate data are given in Table II (supplementary material) and show no dependence on $[Fe(\alpha_4\text{-TMNP})]_T$ below pH 4 (thereby reflecting k_h only) but a dependence on $[Fe(\alpha_4\text{-TMNP})]_T$ at higher pHs, thus reflecting contributions from both hydrolysis (k_h) and dimerization (k_f). Provided proton transfers are fast such that the various monomeric species are at

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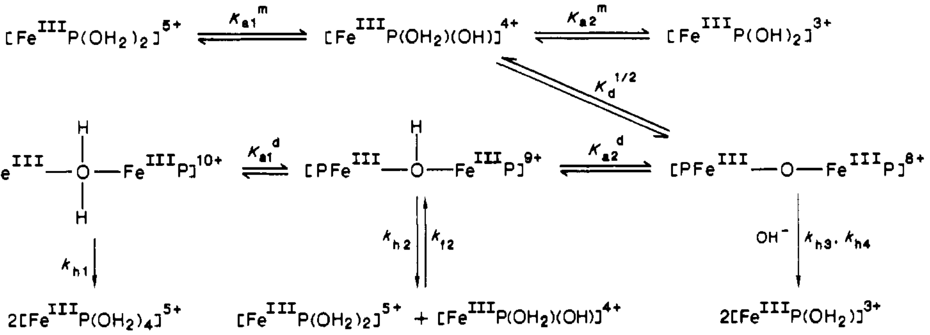
(13) Kurihara, H.; Afifuku, F.; Ando, I.; Saita, M.; Nishino, R.; Ujimoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3515.

(14) Albert, A.; Serjeant, E. P. *Ionization Constants of Acids and Bases, A Laboratory Manual*; Methuen: London, 1962; pp 69–92.

(15) *BMDPAR-Derivative free non linear regression programme*; Department of Biomathematics, University of California: Los Angeles, 1981. This program was converted for use on a VAX-11 computer by Management Science Associates, Pittsburgh, PA, 1982. Data pairs c^{rel}, y, where c^{rel} = relative $[Fe^{III}(TMPyP)]$ based on $c^{rel} = 1$ for the initial porphyrin solution and $y = abs/c^{rel}$, were fitted to the equations $M = \{(0.25 + 2K_dc^{rel})^{1/2} - 0.5\}/2K_d$ and $y = (\epsilon_m{}^{rel} + \epsilon_d{}^{rel}K_dM_e{}^2)/c^{rel}$, where M_e represents the equilibrium monomer concentration and $\epsilon_m{}^{rel}$ and $\epsilon_d{}^{rel}$ are relative extinction coefficients of the monomer and dimer, respectively. ($\epsilon_m{}^{rel}$ = 68.1 (520 nm), 56.6 (536), 69.4 (507); $\epsilon_d{}^{rel}$ = 46.1 (520), 43.6 (536), 64.3 (597).)

Scheme I



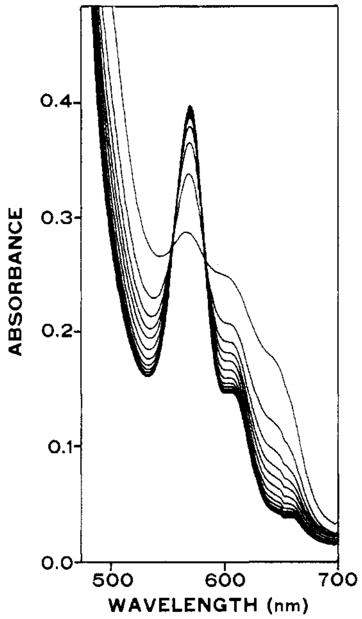


Figure 3. Spectral changes following the pH jump of a solution of $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$ (4.77×10^{-5} mol dm^{-3}), initially at pH 3.0, to pH 7.69 ($I = 0.01$ mol dm^{-3} ($NaNO_3$), 25 °C). Successive spectra were recorded at 2-min intervals.

equilibrium, this process is of the type $D \rightleftharpoons 2M$. For small perturbations the relaxation expression (8) is obeyed[16] ($[M]_e$

$$\tau^{-1} = k_{obsd} = 4k_f[M]_e + k_h \qquad (8)$$

represents the equilibrium monomer concentration). k_{obsd} data (Table II) were so analyzed with the listed k_h values being those obtained from the intercepts at $[M]_e = 0$. However, when a solution of the monomer $[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+} > 4 \times 10^{-5}$ mol dm^{-3} at pH 3.0 is jumped to pH >5.6, the equilibrium position now favors the μ-oxo dimer. Figure 3 shows such a second-order approach to equilibrium at pH 7.69. This process was investigated over the pH range 5.52–7.69 and for $[FeP]_T = (4.47\text{–}6.55) \times 10^{-5}$ mol dm^{-3}. Second-order rate constants (k_f) were obtained from linear plots of $([M]_t - [M]_e)^{-1}$ vs time, and these are given in Table III (supplementary material).

The reaction of the TMPyP dimer $[\{Fe(TMPyP)\}_2O]^{8+}$ was similarly studied with first-order data being obtained over the complete pH range 1–13. Those data from pH 1 to 6, and those above pH 10.5, were independent of dimer concentration (7.5×10^{-5}, 3.57×10^{-5} mol dm^{-3}) and therefore represent k_h. Such data are given in Table IV (supplementary material). For the pH range 6–10.5 the data (Table V, supplementary material) show a concentration dependence and therefore contain both k_h and k_f. Under such conditions the more generally useful expression (9)[16,17] was

$$\tau^{-2} = k_{obsd}^2 = 8k_fk_h[Fe(TMPyP)]_T + k_h^2 \qquad (9)$$

used. This does not require a prior knowledge of K_d and uses only the total substrate concentration. Plots of k_{obsd} vs $[Fe(TMPyP)]_T$ were linear, and values of k_f and k_h are listed in Table V. The average k_f/k_h value (6.7×10^3 mol^{-1} dm^3) represents K_d, and this agrees reasonably well with that obtained from the direct spectral measurement at pH 7.45 ($(7.35 \pm 0.10) \times 10^3$ mol^{-1} dm^3).

Discussion

Hydrolysis and Dimerization Equilibria. The equilibrium, kinetic, and electrochemical data[39] support the existence of three monomeric, and up to three dimeric, species for the iron(III) porphyrins with P = α_4-TMNP and TMPyP in aqueous solution. Scheme I depicts these. Only three monomeric ions exist for the P = $\alpha\beta\alpha\beta$-TMNP system. The protonated dimers $[\{Fe(P)\}_2OH]^{9+}$ and $[\{Fe(P)\}_2OH_2]^{10+}$ were not directly observed although significant quantities of $[\{Fe(TMPyP)\}_2OH]^{9+}$ are required by the kinetic results in the pH range 4–6.

Our equilibrium data are compared with literature data in Table VI. The acidities of $[Fe(P)(OH_2)_2]^{5+}$, P = $\alpha\beta\alpha\beta$-TMNP ($pK_{a_1}{}^m$ = 6.09), P = α_4-TMNP (5.79), and P = TMPyP (5.79), are similar with these highly positively charged metalloporphyrins being more acidic than those of lower positive, or negative, charge. The $pK_{a_2}{}^m$ values for P = $\alpha\beta\alpha\beta$-TMNP (10.28) and α_4-TMNP (10.0) show that their aqua–hydroxo ions are more acidic than $[Fe(TMPyP)(OH_2)(OH)]^{4+}$ ($pK_{a_2}{}^m$ = 11.71), suggesting that coordination to the second water molecule in the latter is appreciably weaker.

Few certain deprotonations of a second coordinated water have been observed with monomeric iron(III) systems (cf. Table VI). This is usually because dimerization is both rapid and reasonably complete at high pH. Also, it is suggested from this study that the spectral changes associated with a second deprotonation may not be overly large (Figure 1). Such weak acidity of a second coordinated water supports the generally accepted view of a distorted coordination environment with the Fe(III) atom being held somewhat out of the porphyrin plane toward the other electronegative ligand (by up to 50 pm for OH^-, Cl^-, OMe^-).[18,19] It is unlikely that the water molecules in $[Fe(P)(OH_2)_2]^{5+}$ are replaced by electrolyte anions since spectra obtained with the same concentrations of NaCl, NaBr, $NaNO_3$, and NaO_3SCF_3 were indistinguishable, whereas significant changes did occur with F^-, N_3^-, CN^-, and SCN^-. Also, the structure of $[Fe(TMPyP)(OH_2)_2]Br_5$ in the solid state clearly contains two trans-coordinated water molecules.[20] Whether or not the monohydroxo system has its sixth coordination site occupied by water is less certain,[4] but we prefer to include it since the corresponding cobalt(III) complex $[Co(TMPyP)(OH_2)_2]^{5+}$ has similar $pK_{a_1}{}^m$ and $pK_{a_2}{}^m$ values (5.5

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(16) Bernasconi, C. F. *Relaxation Kinetics*; Academic: London, 1976.

(17) It can be shown[21] that for an error of <5% in τ^{-1} the criterion $\Delta[M]_T < 0.2([M]_e + K_d^{-1})$ must be obeyed, where $\Delta[M]_T$ represents the change in total monomer concentration ($[Fe(TMPyP)(OH_2)_2]^{5+}$ + $[Fe(TMPyP)(OH_2)(OH)]^{4+}$ during the reaction. It was shown that this criterion was obeyed up to $[Fe(TMPyP)]_T \approx 10^{-4}$ mol dm^{-3}, the maximum concentration of iron(III) porphyrin used in these studies.

(18) Hoard, J. L. *Science (Washington, D.C.)* **1971**, *174*, 1295.

(19) Fleischer, E. B. *Acc. Chem. Res.* **1970**, *3*, 105.

(20) Robinson, W. T., private communication. A crystal structure of $[Fe(TMPyP)(OH_2)_2]Br_5{\cdot}xH_2O$ has been completed and will be reported shortly.

Table VI. Equilibrium Data for Water-Soluble Monomeric and Dimeric Iron(III) Porphyrins and Related Systems (25 °C)

	monomeric species		dimeric species				
species[a]	$pK_{a_1}{}^m$	$pK_{a_2}{}^m$	$\log K_d$	$pK_{a_2}{}^d$	$pK_{a_1}{}^d$	conditions	ref
$[Fe(TSPP)(OH_2)_2]^{3-}$	7.0		5.9	~6.4	*b*	0.1 M $NaNO_3$	*c*
				8.5		0.1 M NaCl	*d*
$[Fe(TSDMPP)(OH_2)_2]^{3-}$	7.25	>14	none found			0.2 M $NaNO_3$	*o*
$[Fe(DSDPIX)(OH_2)_2]^{3-}$	7.7		6.5				*e*
$[Fe(DCMPIX)(OH_2)_2]^{3-}$	7.49		5.0				*f*
$[Fe(DPIX)(OH_2)_2]^-$	7.1		5.6	7.4			*g*
$[Fe(TCPP)(OH_2)_2]^{4-}$	6.72	9.58					*h*
$[Fe(PPIX)(OH_2)_2]^-$	6.63		7.3	7.5			*i, g*
$[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$	6.09	10.28	<2 (none found)			0.1 M $NaNO_3$	*j*
$[Fe(\alpha_4\text{-TMNP})(OH_2)_2]^{5+}$	5.79	10.0	7.26	<2		0.1 M $NaNO_3$	*j*
$[Fe(TMPyP)(OH_2)_2]^{5+}$	5.79	11.71	3.87	5.45	<2	0.1 M $NaNO_3$	*j*
				5.9		0.1 M NaCl	*d*
	5.5	~11.5	3.3			0.05 M buffer	*k*
	5.7	12.3				0.05 M Na_2SO_4	*l*
	5.5	~12				0.1 M Na_2SO_4, 30 °C	*m*
	5.35		~5.9			0.05 M $NaNO_3$	*p*
$[Fe(3\text{-TMPyP})(OH_2)_2]^{5+}$	6.0	12.2				0.05 M Na_2SO_4	*n*
$[Fe(2\text{-TMPyP})(OH_2)_2]^{5+}$	5.4	10.0				0.05 M Na_2SO_4	*n*
$[Fe(TEnPPIX)(OH_2)_2]^{5+}$	5.12		5			0.05 M $NaNO_3$	*p*
$Fe(EDTA)(OH_2)$	7.58		5				*q*
$Fe(AEDTA)(OH_2)$	4.11	8.69					*q*
$[Fe(H_2O)_6]^{3+}$	2.8						*r*

[a] In all cases the monomeric diaqua complex appears to be the only species existing at dilute concentrations in acidic aqueous solution. In several cases this has been designated as a monoaqua complex. The coordinated porphyrin dianion is defined in ref 2. [b] A pathway for hydrolysis of the doubly protonated dimer was observed, but such species appear to have only transient existence and are very acidic. [c] El-Awady, A. D.; Wilkins, P. C.; Wilkins, R. G. *Inorg. Chem.* **1985**, *24*, 2053. [d] Harris, F. L.; Toppen, D. L. *Inorg. Chem.* **1978**, *17*, 71. [e] Kolski, G. P.; Plane, R. A. *Ann. N.Y. Acad. Sci.* **1973**, *206*, 604. [f] Goff, H.; Morgan, L. O. *Inorg. Chem.* **1976**, *15*, 2062. The μ_{eff_g} value of 5.5 μ_B for solutions of the dimer is inconsistent with the expected antiferromagnetic coupling. [g] Brown, S. B.; Dean, T. C.; Jones, P. *Biochem. J.* **1970**, *117*, 733. Jones, P.; Prudhoe, K.; Brown, S. B. *J. Chem. Soc., Dalton Trans.* **1974**, 911. (The K_d determination ($n = 1$) assumed only one monomeric species to be present at the pH of measurement.) [h] Strong, J. D.; Hartzell, C. R. *Bioinorg. Chem.* **1976**, *5*, 219. These authors believed they were dealing with the dimer, but it is clear from the concentrations used and from the visible and ESR spectra that the monomeric species was in fact being studied. [i] Hasinoff, B. B.; Dunford, H. B.; Horne, D. G. *Can. J. Chem.* **1969**, *47*, 3225. This reference gave measurements of $pK_{a_1}{}^m$ in 44.5% ethanol–55.5% water against a pH* scale. [j] This work. [k] Tondreau, G. A.f Wilkins, R. G. *Inorg. Chem.* **1986**, *25*, 2745. [l] Kobayashi, N.; Koshiyama, M.; Osa, T.; Kuwana, T. *Inorg. Chem.* **1983**, *22*, 3608. [m] Kurihara, H.; Arifuku, F.; Ando, I.; Saito, M.; Nishino, R.; Ujimoto, K. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3515. [n] Kobayashi, N. *Inorg. Chem.* **1985**, *24*, 3324. [o] Zipplies, M. F.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 4433. [p] Pasternack, R. F.; Lee, H.; Malek, P.; Spencer, C. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1865. $pK_{a_1}{}^m$ values were recalculated by assuming a single deprotonation and $\epsilon(403\ nm) = 4.15 \times 10^4\ mol^{-1}\ dm^3\ cm^{-1}$ for $[Fe(TMPyP)(OH_2)(OH)]^{4+}$. [q] Gustafson, R. L.; Martell, A. E. *J. Phys. Chem.* **1963**, *67*, 576. [r] Milburn, R. M.; Voshurg, W. C. *J. Am. Chem. Soc.* **1955**, *77*, 1352.

and 10.7)[21] and octahedral coordination is almost certain for $[Co(TMPyP)(OH)(OH_2)]^{4+}$.

The tendency for iron(III) porphyrins to aggregate via π-interactions of the porphyrin rings[22] or to dimerize via μ-oxo formation[23] is well-known, but with suitable protection (i.e. double-"picket fenced" porphyrins) this can be restricted, and even prevented.[24] The present porphyrins demonstrate the effect of porphyrin structure on the ability to dimerize with log K_d values decreasing, 7.26 for α_4-TMNP (one unhindered face), 3.87 for TMPyP (both faces unhindered), and <2 (not observed) for $\alpha\beta\alpha\beta$-TMNP (both faces restricted). The only other known water-soluble iron(III) porphyrin to not dimerize in neutral or alkaline aqueous solution appears to be the (tetrakis(2,6-dimethyl-3-sulfonatophenyl)porphyrinato)iron(III) trianion recently reported by Zipplies, Lee, and Bruice.[25]

Our log K_d value for P = TMPyP (3.87) agrees reasonably well with that obtained by Tondreau and Wilkins (3.3) at the lower ionic strength[4] and with the earlier values of 3.73 (0.5 mol dm^{-3}, NaCl)[26] and 3.34 (0.1 mol dm^{-3}, KCl)[27] obtained from magnetic and electrochemical investigations. Comparison with the value of 5.9 for the P = $TSPP^{4-}$ system[3] shows that overall charge plays some role. We found no spectrophotometric (or electrochemical) evidence for deprotonation of the μ-oxo dimers in the α_4-TMNP or TMPyP systems at high pH (to 0.1 mol dm^{-3} OH^-) and therefore support the view[3,4] that $[\{Fe(P)\}_2O]^{8+}$ species are five-coordinate. A crystal structure under way on $[\{Fe(TMPyP)\}_2O](NO_3)_8$[28] should clarify this point.

Both the acidity and the dimerization constants are very sensitive to variations in ionic strength. Thus, $pK_{a_1}{}^m$ for $[Fe(\alpha\beta\alpha\beta\text{-TMNP})(OH_2)_2]^{5+}$ changes from 5.88 in 0.05 mol dm^{-3} $NaNO_3$ to 6.72 in 1.0 mol dm^{-3} $NaNO_3$ (Table I), and $[\{Fe(TMPyP)_2\}O]^{8+}$ is stabilized as the ionic strength is raised ($K_d \approx 2 \times 10^2$ in 0.004 mol dm^{-3} $NaNO_3$,[1] 7.35×10^3 in 0.10 mol dm^{-3} $NaNO_3$). Substantial ionic strength effects have been noted previously with $[Fe(PPIX)(OH_2)_2]^-$,[29] so that highly charged synthetic porphyrins are not the only ones at risk. These effects warrant a detailed investigation in their own right since they undoubtedly influence the behavior of similar species in biological systems.

The large K_d values (Table VI) emphasize the well-known propensity for Fe(III) complexes to dimerize in neutral or slightly alkaline aqueous solution (pH 6–9). Only at pH <4 and >10 do monomeric diaqua and dihydroxo ions assume significance. Thus, species such as $[Fe(P)(OH_2)(OH)]^{n+}$ are relatively unimportant in an equilibrium sense, but they do assume a vital role in the dimerization mechanism.

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(21) Ashley, K. R.; Hu-Young, S. *Inorg. Chem.* **1976**, *15*, 1937.

(22) (a) White, W. I.; Plane, R. A. *Bioinorg. Chem.* **1974**, *4*, 21. (b) Goff, H.; Morgan, L. O. *Inorg. Chem.* **1976**, *15*, 2062. (c) Abraham, R. J.; Evans, B.; Smith, K. M. *Tetrahedron* **1978**, *34*, 1213 and references cited therein.

(23) (a) White, W. I. In *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979; Vol. V, Chapter 7. (b) See ref 29b in: Krishnamurthy, M.; Sutter, J. R.; Hambright, P. *J. Chem. Soc., Chem. Commun.* **1975**, 13.

(24) Cheng, R. J.; Latos-Grazynski, L.; Balch, A. L. *Inorg. Chem.* **1982**, *21*, 2412.

(25) Zipplies, M. F.; Lee, W. A.; Bruice, T. C. *J. Am. Chem. Soc.* **1986**, *108*, 4433.

(26) Goff, H.; Morgan, L. O. *Inorg. Chem.* **1976**, *15*, 3181.

(27) Forshey, P. A.; Kuwana, T. *Inorg. Chem.* **1981**, *20*, 693.

(28) Crystals of $[\{Fe(\alpha_4\text{-TMNP})\}_2O](NO_3)_8 \cdot xH_2O$ suitable for X-ray analysis have been supplied to Dr. W. T. Robinson.

(29) Blauer, G.; Ehrenberg, A. *Biochem. Biophys. Acta* **1966**, *112*, 496.

Table VII. Rate Constants for the Formation and Hydrolysis of Water-Soluble Dimeric Iron(III) Porphyrins (25 °C)

species[a]	k_{f_2}, $mol^{-1}\ dm^3\ s^{-1}$	k_{h_2}, s^{-1}	K_d,[b] $mol^{-1}\ dm^3$	$k_{h_1}(K_{a_1}{}^d)^{-1}$, $mol^{-1}\ dm^3\ s^{-1}$	conditions	ref
$[\{Fe(TSPP)\}_2O]^{8-}$	1.5×10^6	8.0	7.5×10^5	*d*	0.1 M $NaNO_3$	*e*
		2.69			0.1 M NaCl	*f*
$[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$	1.2×10^4	>40[j]	2.2×10^7	*i*	0.01 M $NaNO_3$	*g*
$[\{Fe(TMPyP)\}_2O]^{8+}$	1.06×10^3	0.355	6.5×10^3	26.6	0.1 M $NaNO_3$	*g*
	0.9×10^3				0.05 M buffer	*h*
		0.155			0.10 M NaCl	*f*

[a] The nonprotonated oxo species is the stable entity in aqueous solution. [b] $K_d = (k_{f_2}/k_{h_2})(K_{a_2}{}^d/K_{a_1}{}^m)$. [c] Since the doubly deprotonated dimer $[\{Fe(P)\}_2OH_2]^{10+}$ is very acidic ($pK_{a_1}{}^d < 1$), the limiting first-order rate for hydrolysis of this species has not been observed. [d] Noted but not analyzed in detail (footnote *e*). [e] Reference 3. [f] Reference 6. [g] This work. [h] Reference 4. [i] This process is likely to occur in very acidic media, but (possibly) because of overlapping $K_{a_1}{}^d$ and k_{h_1} values it cannot be distinguished kinetically (cf. text). [j] Calculated by assuming $pK_{a_2}{}^d \leq 2$ (see text).

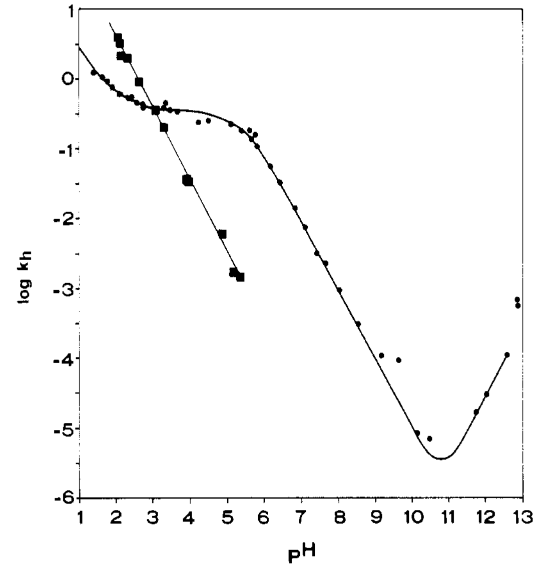
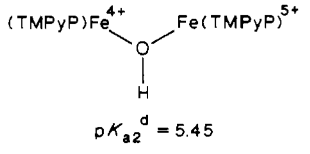


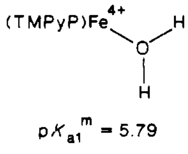
Figure 4. Variation in observed first-order rate constants for hydrolysis of the dimers (k_h) vs pH: (■) $Fe(\alpha_4\text{-TMNP})^{n+}$ system (data from Table II, $I = 0.01$ mol dm^{-3} ($NaNO_3$), 25 °C); (●) $Fe(TMPyP)^{n+}$ system (data from Tables IV and V, $I = 0.1$ mol dm^{-3} ($NaNO_3$), 25 °C). Solid curves were calculated by using eq 14 and constants given in the text and Table IX.

Hydrolysis and Dimerization Pathways. Rate constants for hydrolysis (k_h, Tables II, IV, and V) and dimerization (k_f, Tables II, III, and V) for the two systems P = α_4-TMNP and TMPyP are plotted as a function of pH in Figures 4 and 5, respectively. Our data for hydrolysis of $[\{Fe(TMPyP)\}_2O]^{8+}$ on the acid side of pH 10 follows closely the combined results of Tondreau and Wilkins,[4] Pasternack and co-workers,[30] and Harris and Toppen.[8] Our data have been analyzed according to expression 10 with $K_{a_2}{}^d$

$$k_h = \frac{k_{h_1}a_{H^+}}{K_{a_1}{}^d} + \frac{K_{h_2}a_{H^+}}{a_{H^+} + K_{a_2}{}^d} + \frac{k_{h_3}K_W}{a_{H^+}} \qquad (10)$$

$= 3.55 \times 10^{-6}$ $mol^{-1}\ dm^3$, $k_{h_2} = 0.355\ s^{-1}$, $k_{h_1}/K_{a_1}{}^d = 26.6\ mol^{-1}\ dm^3\ s^{-1}$, $k_{h_3} = 2.89 \times 10^{-3}\ mol^{-1}\ dm^3\ s^{-1}$, and $K_W = 1.008 \times 10^{-14}\ mol^2\ dm^{-6}$. Agreement is shown by the solid line of Figure 4, and comparisons of kinetic constants are given in Table VII. The acid-independent region, clearly identified from pH 3 to 6, is ascribed to hydrolysis of the monoprotonated bridged complex $[\{Fe(TMPyP)\}_2OH]^{9+}$ (k_{h_2}, Scheme I). The first order in acid region below pH ~2 is ascribed to further protonation of the bridge and hydrolysis of the doubly protonated dimer (k_{h_1}). Comparison of acidities for





infers a similar electron-withdrawing capacity for $Fe(TMPyP)^{5+}$ and H^+, and extension of this analogy to the doubly protonated dimer $[\{Fe(TMPyP)\}_2OH_2]^{10+}$ would suggest a $pK_{a_1}{}^d$ of about -1.7.[31] Likewise, hydrolysis of the related dimeric $[\{Co(NH_3)_5\}_2OH]^{5+}$ ion involves both acid-independent and first order in $[H^+]$ contributions[32] so that multiprotonation of bridged oxo atoms seems a rather general observation for such systems.

Attempts to detect by spectrophotometric means the monoprotonated bridged species failed. The first trace obtained (within 7.6 ms) on rapidly pH-jumping a solution of $[\{Fe(TMPyP)\}_2O]^{8+}$ from pH 10.4 to 4.15 had maxima and absorptions (720–520- and 520–320-nm ranges) indistinguishable from those of the reactant at pH 10.4. Subsequent traces displayed isosbestic points (cf. Figure 1) in agreement with it being a mixture of $[\{Fe(TMPyP)\}_2O]^{8+}$ and $[Fe(TMPyP)(OH_2)_2]^{5+}$. Similarly, the first spectral trace in the Soret region on pH jump $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ from pH 8 to 2.5 was identical with that of the starting material at pH 8. We do not have an adequate explanation for these results as we would have expected a useful spectral change on protonating the bridge. El-Awady, Wilkins, and Wilkins report[3] seeing immediate small spectral changes on acidifying $[\{Fe(TSPP)\}_2O]^{8-}$, but our experience with impure samples of $[\{Fe(TMPyP)\}_2O]^{8+}$ suggests that this may have been due to traces of monomer still present in their initial dimer solution. Our equilibrium titration data for dimerization of both $[Fe(P)(OH_2)_2]^{5+}$ systems (P = α_4-TMNP, TMPyP) require a 2 H^+ stoichiometry, so that the dimeric species must have the composition $[\{Fe(P)\}_2O]^{8+}$.

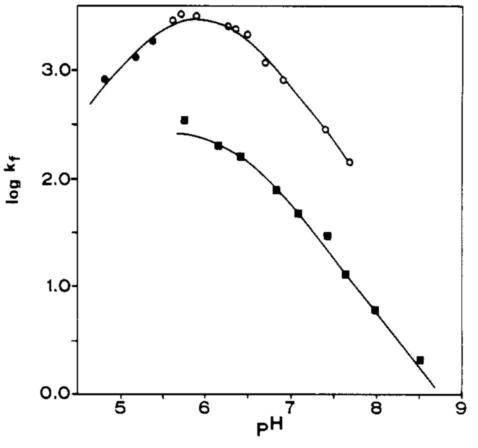


Figure 5. Variation in observed first-order rate constants for dimer formation (k_f) vs pH: (upper trace) $Fe(\alpha_4\text{-TMNP})^{n+}$ system (data from Tables II (●) and III (○), $I = 0.01$ mol dm^{-3} ($NaNO_3$), 25 °C); (lower trace) $Fe(TMPyP)^{n+}$ system (data from Table V, $I = 0.10$ mol dm^{-3} ($NaNO_3$), 25 °C). Solid curves were calculated by using eq 16 and constants given in the text and Table IX.

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(30) Pasternack, R. F.; Lee, H.; Malek, P.; Spencer, C. *J. Inorg. Nucl. Chem.* **1977**, *39*, 1865.

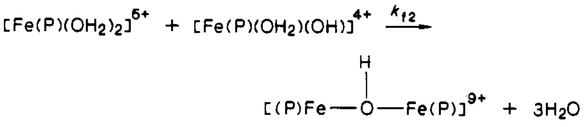
(31) Likewise, comparison of $pK_{a_2}{}^d \approx 6.4$ with $pK_{a_1}{}^m = 7.0$ for the Fe(TSPP) system[3] supports this analogy.

(32) Ellis, J. D.; Scott, K. L.; Sykes, A. G. *Inorg. Chem.* **1972**, *11*, 2562. Wharton, R. K.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1973**, 439. The hydrolysis rate of the μ-hydroxo dimer is some 10^2 slower than that found here: $k_0 = 4.0 \times 10^{-3}\ s^{-1}$; cf.: Buckingham, D. A.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1974**, *13*, 2165.

In strongly alkaline solution (pH >11, Figure 4) an additional path for hydrolysis of $[\{Fe(TMPyP)\}_2O]^{8+}$ is observed. Data at $I = 0.1$ mol dm^{-3} (Table IV) is first-order in a_{OH^-} except at the highest pH, where it falls above the rate predicted by eq 10. This suggests an even higher order term in a_{OH^-}, and other data to 0.5 mol dm^{-3} NaOH support this view. This would be expected if there were a pathway for OH^- attack on the monohydroxo species $[\{Fe(TMPyP)_2O(OH)\}]^{7+}$. The first order in a_{OH^-} term can be ascribed to attack by OH^- at one of the two vacant coordination positions in $[\{Fe(TMPyP)\}O]^{8+}$ if the metal is five-coordinate or to deprotonation and spontaneous hydrolysis if water occupies both remaining coordination sites. We consider the former alternative most likely.

Hydrolysis of $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ follows first order in $[H^+]$ kinetics over the total accessible pH range 2.05–5.3 (Figure 4). The enhanced stability of the dimer prevented useful measurements being made above pH 5.3, and at high alkalinities ($[OH^-] = 0.10$ mol dm^{-3}) this system appeared to be much more stable than $[\{Fe(TMPyP)\}_2O]^{8+}$. The very small spectral changes observed over long times were not those expected for formation of $[Fe(\alpha_4\text{-TMNP})(OH)_2]^{3+}$. The absence of an inflection in the hydrolysis data prevents a $pK_{a_2}{}^{d}$ value from being determined. Since the pH titration data indicate a fully formed deprotonated dimer at pH 3 (2 H^+ were lost in forming the dimer from the diaqua monomer), it follows that $pK_{a_2}{}^{d} < 3$. Two possibilities then exist. Either the parameters combine such as to preclude deprotonation being detected kinetically in the pH range 2–3 (i.e. $k_{h_2}K_{a_1}{}^{d} \approx k_{h_1}K_{a_2}{}^{d}$) or $pK_{a_2}{}^{d} < 2$ with protonation lying outside the experimentally accessible pH range. Similar hydrolytic pathways have been found for other μ-oxo iron(III) systems, including P = TSPP,[3,8,33] and EDTA and CDTA,[34,35] and it appears that $K_{a_2}{}^{d}$ values do vary significantly from system to system.

Formation of the dimers (P = α_4-TMNP and TMPyP) is accommodated by the microscopic reverse of the predominant hydrolysis pathway; viz. by a combination of diaqua and aqua–hydroxo monomers (eq 11). Least-squares fits of the k_f data



$$[Fe(P)(OH_2)_2]^{5+} + [Fe(P)(OH_2)(OH)]^{4+} \xrightarrow{k_{f2}} [(P)Fe{-}\overset{\displaystyle H}{\overset{|}{O}}{-}Fe(P)]^{9+} + 3H_2O \quad (11)$$

(Tables III and V) to (12) are shown by the solid curves of Figure

$$k_f = \frac{k_{f_2}K_{a_1}{}^{m}a_{H^+}}{(K_{a_1}{}^{m} + a_{H^+})^2} \qquad (12)$$

5 ($K_{a_1}{}^{m}$ values, Table I; $k_{f_2} = 1.2 \times 10^4$ (α_4-TMNP), 1.06×10^3 mol^{-1} dm^3 s^{-1} (TMPyP)). Our k_f value for the TMPyP system agrees well with that reported by Tondreau and Wilkins[4] (0.9×10^3 mol^{-1} dm^3 s^{-1} in 0.5 mol dm^{-3} buffer). No kinetic evidence was found for dimerization by two $[Fe(\alpha_4\text{-TMNP})(nOH_2)_2]^{5+}$ units to pH 4.85, and electrochemical data[39] extend the kinetic data for the $[Fe(TMPyP)(OH_2)_2]^{5+}$ systems to pH 2. Unfortunately our stopped-flow apparatus would not handle the high concentrations of $[Fe(TMPyP)(OH_2)_2]^{5+}$ necessary to directly follow dimerization under such conditions. The kinetically determined k_{f_2} and k_{h_2} values (Table VII) allow an alternative measure of $K_d = (k_{f_2}/k_{h_2})(K_{a_2}{}^{d}/K_{a_1}{}^{m})$, and good agreement is found (cf. Tables VI and VII).

The dimerization process involving one diaqua and one hydroxo–aqua unit is that previously described by Wilkins and co-workers (P = TSPP[3] and TMPyP[4]). It is to be contrasted with the slow dimerization by two [Fe(TMPP)(OH)] units in alkaline CCl_4 solution, for which Fielding, Eaton, and Eaton propose rate-limiting dissociation of OH^- to form a reactive four-coordinate intermediate.[36] Wilkins[3] discusses dimerization in terms of prior (non-rate-determining) loss of water from $[Fe(P)(OH_2)(OH)]$. An obvious alternative is for iron(III) to extend its coordination sphere by direct attack of metal-bound hydroxide in $[Fe(P)(OH_2)(OH)]^{4+}$ on $[Fe(P)(OH_2)_2]^{5+}$ and to subsequently or concurrently lose water from the seven-coordinate intermediate or transition state. The nucleophilic tendencies of M^{III}–OH species are well-known,[37] as is the ability of Fe(III) to extend its coordination sphere (viz. $[Fe(EDTA)(OH_2)]^-$ is pentagonal bipyramidal in the solid state and may adopt higher coordination in solution[38]).

Comparisons of rate constants (Table VII) show that the increased stability of $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ compared to the P = TMPyP and TSPP systems ($\log K_d = 7.26$ (α_4-TMNP), 3.87 (TMPyP), and 5.9 (TSPP)) resides largely in the increased acidity of the protonated dimer ($pK_{a_2}{}^{d} < 3$ (α_4-TMNP) and $pK_{a_2}{}^{d} = 5.45$ (TMPyP), 6.4 nTPPS)[3]). The formation rate constant for the α_4-TMNP monomer lies between those found for the TSPP and TMPyP systems ($k_{f_2} = 1.2 \times 10^4$ (α_4-TMNP), 1.5×10^6 (TSPP), 1.06×10^3 mol^{-1} dm^3 s^{-1} (TMPyP)), possibly because metal-bound hydroxide in $[Fe(\alpha_4\text{-TMNP})(OH_2)(OH)]^{4+}$ is intermediate in its nucleophilic ability. The hydrolysis rate constant for the protonated dimer $[\{Fe(\alpha_4\text{-TMNP})\}_2OH]^{9+}$ appears to be substantially greater than those for the corresponding P = TSPP, TMPyP systems ($k_{h_2} > 40$ (α_4-TMNP), 8.0 (TSPP),[3] 0.36 s^{-1} (TMPyP)).

Supplementary Material Available: Observed rate constants for the hydrolysis and relaxation of $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ at pH 2.05–5.32 (Table II), for the formation of $[\{Fe(\alpha_4\text{-TMNP})\}_2O]^{8+}$ at pH 5.64–7.69 (Table III), for the hydrolysis of $[\{Fe(TMPyP)\}_2O]^{8+}$ at pH 1.38–10.48 and 0.01–0.50 mol dm^{-3} NaOH (Table IV), and for the relaxation of $[\{Fe(TMPyP)\}_2O]^{8+}$ at pH 5.75–9.62 (Table V) (6 pages). Ordering information is given on any current masthead page.

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