the material in its pure state but have confirmed its structure *via* its chemical reactions (*vide infra*). Thus the white sublimate, obtained upon treatment of 1,4-dimethoxyhexamethyl-*p*-disiline[3] with acetyl chloride followed by removal of methyl acetate and excess acetyl chloride, was reconverted to 1,4-dimethoxyhexamethyl-*p*-disiline in an exothermic reaction with methanol and triethylamine. The dichloride was also prepared by Atwell.[14]

1,4-Dihydroxyhexamethyl-*p*-disiline. Acetyl chloride (2 cm^3) was heated to reflux overnight with 450 mg of 1,4-dimethoxyhexamethyl-*p*-disiline. The excess acetyl chloride and methyl acetate were removed under vacuum. The residue was dissolved in 30 cm^3 of dry tetrahydrofuran (distilled from LAH and used immediately). To this solution was added, with stirring, 0.5 cm^3 of triethylamine (distilled from phenyl isocyanate) and 0.04 cm^3 of water in 30 cm^3 of dry THF. The mixture was allowed to stir overnight at room temperature. After the triethylamine hydrochloride was removed by filtration, the solvent was removed to afford the dihydroxide in quantitative yield. The white solid sublimes at 230°, is soluble in MeOH and DMSO, slightly soluble in ether, and insoluble in petroleum ether: mass spectrum (*m/e*) 228 (parent, 20%) 213 (M − 15, 70%), 195 (50%), 173 (100%), 159 (80%), 119 (50%), 97, 99 (20%), 75 (60%), 61 (20%), 45 (60%); nmr (DMSO-d_6, δ, external TMS) 0.05 (s, 6), 1.8 (s, 12), 3.4 (s, 1), 5.45 (s, 1). Therefore the dihydroxide exists as a 50/50 cis–trans mixture of isomers, where the difference in chemical shift between the isomeric hydroxyl hydrogens is ~2 ppm. Glpc (2-ft, 0.25-in. 10% SE-30 on silanized chromosorb W 30–60 mesh) showed two peaks of approximately equal intensity.

Dodecamethyldioxa[1.1]di-*p*-disilinocyclophane. Into a small, dry sublimer were placed 0.519 g of 1,4-dimethoxyhexamethyl-*p*-disiline and 1 cm^3 of acetyl chloride. The mixture was heated to reflux overnight. The volatile components were then evaporated under a fast stream of dry argon gas and the residue was sublimed at 70° (1 mm). The sublimer pot was exchanged quickly and the sublimate was washed into the new pot with 15 cm^3 of dry THF. The THF solution was treated with 0.25 cm^3 of hydrazine and allowed to sit for 48 hr. Upon evaporation of the solvent, the residue was washed several times with ether. The ether washings were stored at −15° overnight and deposited 20–50 mg of colorless, hexagonal prisms (sublimation point >268°). The compound is slightly soluble in THF, DMSO, and ether and insoluble in petroleum ether. Glpc (2 ft × 0.25 in. column; 10% SE-30 on silanized chromosorb W 30–60 mesh; injection, 300°; column, 200°; detection, 300°) showed a single component. Elemental analysis was done *via* mass spectroscopy.[15] *Anal.* Calcd for $C_{20}H_{36}O_2Si_4$: 420.1801. Found: 420.1792; error, 2 ppm. Nmr (CS_2, δ relative to TMS internal standard) 0.15 (s, 1), 1.7 (s, 2); ir (KBr) 2950, 1250, 1012, 850 cm^{-1}.

A dilute THF solution of freshly prepared 1,4-dichlorohexamethyl-*p*-disiline (*vide supra*) was treated with a dilute THF solution of 1,4-dihydroxyhexamethyl-*p*-disiline (mixture of isomers). Triethylamine was added and the mixture stirred overnight. Glpc analysis (*vide supra*) indicated the presence of **1** plus telomers.

Electron Spin Resonance Spectroscopy. The green radical anion was prepared by reduction of ~2 mg of **1** with a potassium mirror in 1,2-dimethoxyethane (DME) under high vacuum. The potassium mirror was prepared by five consecutive distillations of the metal under vacuum and the DME was dried over sodium–potassium alloy under vacuum until a stable blue color from the dissolving metal was obtained.

The esr spectra were recorded on a Varian-4502 spectrometer equipped with a 12-in. magnet and variable-temperature control. They were calibrated with a Ventron G-502 gaussmeter. Simulated spectra were calculated on a CDC-6400 computer using a suitably modified SESRS[10] program.

Acknowledgment. We acknowledge support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society. We also wish to thank Mr. Patrick Gallagher for recording the esr spectra and the SUNY institutional fund for computer time. The mass spectra and exact mass measurements were performed by the Battelle Memorial Institute Mass Spectrometry Laboratory under the sponsorship of Professor A. Padwa's NIH grant.

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[14] W. H. Atwell, private communication.

[15] Mass spectrum and computer work done by Battelle Memorial Institute; *cf.* Acknowledgment.

Thermodynamic and Kinetic Properties of an Iron–Porphyrin System

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Abstract: The synthesis and characterization of an iron (ferric)-porphyrin monomer and dimer system are described in this paper. A water-soluble porphyrin—the tetrasulfonated tetraphenylporphine (TPPS)—was employed to study the system in aqueous solutions. The magnetic susceptibility and visible absorption spectra of both the iron monomer tetraphenylporphine and the iron monomer of the sulfonated tetraphenylporphine were studied; the dimers of both these systems were also studied. The comparison of the data of the sulfonated and nonsulfonated tetraphenylporphine systems has led to the assignment to both of a monomer Fe^{III}TPPS species and of an oxo-bridged dimer species in aqueous solutions. The equilibrium constant of the dimerization was determined at constant ionic strength ($\mu = 0.10$) and found to be (25°) $K_D = 0.79 \times 10^{-8}\ M$, where K_D is defined by $2Fe^{III}(OH_2)TPPS \rightleftharpoons O\text{-}[Fe^{III}TPPS]_2 + 2H^+ + H_2O$ (K_D). The rate of breakdown of the dimer into monomer (at $\mu = 0.10$, 25°) was studied and led to a rate law $d[\text{dimer}]/dt = \{k_{21} + k_{21}'[H^+]\}[(FeTPPS)_2O]$, with $k_{21} = 41\ \text{sec}^{-1}$ and $k_{21}' = 840\ M^{-1}\ \text{sec}^{-1}$.

The iron–porphyrin system is central to the functioning of many biological systems and thus an understanding of the chemical and physical properties of this system is desirable. The relation of the structural aspects of metalloporphyrins to some of their properties has recently been reviewed.[1] This paper continues the study of the chemistry of a water-soluble porphyrin ligand[2] when it is complexed to iron(III).

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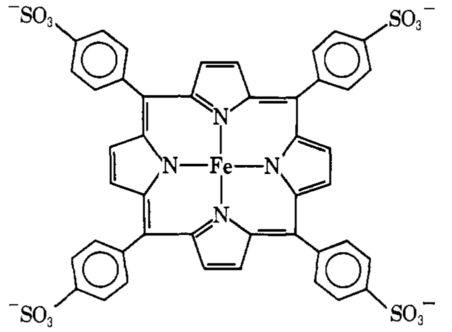
[1] E. B. Fleischer, *Accounts Chem. Res.*, **3**, 105 (1970).

[2] E. B. Fleischer, *Inorg. Chem.*, **1**, 493 (1962); E. B. Fleischer, E. Choi, P. Hambright, and A. Stone, *ibid.*, **3**, 1284 (1964); E. B. Fleischer, S. Jacobs, and S. Mestichelli, *J. Amer. Chem. Soc.*, **90**, 2527 (1968).

The water-soluble porphyrin employed in this study is a sulfonated tetraphenylporphine,[3] which exhibits a high solubility in aqueous solutions and, as far as we can demonstrate, exists in solution as a well-behaved nonaggregated molecular species in pH ranges above 3.0 (see structure I.)



I, Fe^{III}TPPS

The iron(III)–porphyrin system can exist as both a monomer and a dimer in both solution and the solid state. This paper discusses the synthesis and characterization of iron sulfonated tetraphenylporphine and a study of some of the thermodynamic and kinetic properties relating the monomer and dimer species in aqueous solution.

Experimental Section

Tetraphenylporphineiron(III) Chloride. FeTTPCl. $FeCl_2 \cdot 4H_2O$ (2 g) and tetraphenylporphine[4] (abbreviated from here on in as TPP) (5 g) were dissolved in 500 ml of dimethylformamide and the solution was heated at about 140° for 5 or 6 hr. The completion of the reaction was checked spectrophotometrically. The reaction mixture was evaporated to dryness on a steam bath and then dissolved in chloroform; this chloroform solution was shaken with a few milliliters of concentrated HCl. The solution was concentrated to dryness in a flash evaporator. It was again dissolved in chloroform and chromatographed on a dry activated alumina column using $CHCl_3$ as an eluting agent. The first fraction is TPP and the second fraction is the FeTPPCl. The FeTTPCl was recrystallized from xylene. The overall yield was about 70–80%.

Anal. Calcd for $C_{44}H_{28}N_4FeCl$: C, 75.06; H, 4.00; N, 7.96; Fe, 7.93; Cl, 5.04. Found: C, 74.67; H, 4.17; N, 8.05; Fe, 7.79; Cl, 4.95.

μ-Oxo-bis[tetraphenylporphineiron(III)]. O-(FeTPP)$_2$. FeTPPCl (0.5 g) was dissolved in 60 ml of $CHCl_3$. Potassium hydroxide solution (50 ml, 25%) was added and the mixture stirred for 1 hr. The chloroform layer was separated from the water layer and chromatographed twice on a column packed with dry activated alumina and eluted with chloroform. The first fraction which came off the column was FeTPPCl; the second fraction was O-(FeTPP)$_2$ dimer, which was crystallized from a xylene–chloroform mixture. The crystals were collected and washed with petroleum ether (30–60°).

Anal. Calcd for O-(FeTPP)$_2$·xylene, $C_{96}H_{66}N_8OFe_2$: C, 79.01; H, 4.54; N, 7.75; O, 1.10; Fe, 7.75. Found: C, 79.20; H, 4.49; N, 7.78; O, 0.80; Fe, 7.66.

The O-(FeTPP)$_2$ dimer can also be prepared by using 4-picoline (10 ml) as the base instead of NaOH and processed in the same manner as above.

Anal for this batch. Found: C, 79.22; H, 4.47; N, 7.89; O, 0.67; Fe, 8.03.

Tetraphenylporphinemanganese(III) Chloride. MnTPPCl. $MnCl_2 \cdot 4H_2O$ (1.9 g) and TPP (3 g) were dissolved in 300 ml of glacial acetic acid containing 90 ml of acetic anhydride. The mixture was heated for 4 hr at 105–110° on a hot plate with stirring. The completion of the reaction was followed spectrophotometrically. The solution was evaporated to dryness on a steam bath and the resulting solid dissolved in a minimum amount of $CHCl_3$. The solution was chromatographed on a column packed with dry activated alumina and eluted with chloroform. The first fraction which came off the column was the TPP free base and the second fraction was the MnTPPCl. It was crystallized from xylene.

Anal. Calcd for $C_{44}H_{28}N_4MnCl$: C, 75.15; H, 3.98; N, 7.95; Mn, 7.81; Cl, 5.05. Found: C, 75.68; H, 4.04; N, 7.80; Mn, 7.52; Cl, 4.83.

μ-Oxo-bis[tetraphenylporphinemanganese(III)]. O(MnTPP)$_2$. MnTPPCl (0.5 g) was dissolved in 100 ml of pyridine. Potassium hydroxide solution (10 ml, 30%) was added and the mixture was evaporated to dryness on a steam bath. The solid was washed with water to remove the alkali. The above process was repeated twice more. The final dried solid was dissolved in benzene and filtered. The filtrate was concentrated in a conical flask on a steam bath and placed aside for crystallization. The crystals were collected and dried in a vacuum desiccator over anhydrous $CaCl_2$.

Anal. Calcd for O-(H_2OMnTPP)$_2$, $C_{96}H_{70}N_8O_3Mn_2$: C, 76.20; H, 4.36; O, 3.46; N, 8.07; Mn, 7.91. Found: C, 75.71; H, 3.98; O, 4.75; N, 8.15; Mn, 7.67.

Tetraammonium Tetra(*p*-sulfophenyl)porphine. TPPS. Pure TPP (2 g) and concentrated H_2SO_4 (20 ml) were ground into a homogeneous paste with a mortar and pestle. The paste was transferred to a 250-ml beaker and 50 ml of concentrated H_2SO_4 added. The mixture was heated on a steam bath for 4 hr and then allowed to stand at room temperature for 48 hr. The mixture was filtered through a sintered glass frit to remove a small quantity of unreacted TPP. The filtrate was cautiously diluted with two volumes of distilled water. The resulting bright green precipitate is the HSO_4^- salt of the para-sulfonated diacid of TPP. The diacid was washed several times with acetone and then dissolved in methanolic ammonia. The sulfonated porphyrin was precipitated as the ammonium salt by the addition of three volumes of acetone. The porphyrin salt was dried and purified by six successive reprecipitations from methanol solution with acetone.

Anal. Calcd for TPP$(SO_3)_4(NH_4)_4 \cdot 9H_2O$, [$C_{44}H_{36}N_8O_{12}S_4 \cdot 9H_2O$]: C, 44.23; H, 4.17; N, 9.66; S, 10.80. Found: C, 44.22; H, 4.52; N, 9.38; S, 10.72.

The combustion of these compounds always left a small residue which presumably is some sulfate salt. An insufficient period of sulfonation will result in the mono-, di-, and trisulfonated porphyrins as well as the tetrasulfonated porphyrin. The purity of the precipitation may be checked by chromatography on silica gel (Mallinkrodt Chromar 500), using the chloroform phase of a mixture of pyridine:chloroform:water (2:1:1) as the eluent.[3] The tetrasulfonated porphyrin has an R_F value of 0.345, while the mono-, di-, and trisulfonated porphyrins have larger R_F values.

The confirmation that the sulfonations have taken place in the para position was done by nmr. The nmr of the TPPS in D_2O shows an absorption due to the β pyrroles at τ 2.19 and two doublets due to the phenyl protons centered at τ 2.79 and 1.81 with a coupling between them of 8 cps (coupling constant checked by taking the spectrum on both 60- and 100-Mc machines). The integrated area of the phenyl protons to β-pyrrole protons gave the expected 2:1 ratio. The spectrum is of the AX type. It should be an AA′XX′, but the resolution is not high enough to see the other smaller coupling. The nmr is definite evidence for sulfonation occurring at the para position on all four phenyl rings of the TPP.

The TPPS in both neutral and basic pH ranges obeys Beer's law very well. At the neutral pH of 7.0 the TPPS obeys Beer's law at both ionic strength ~0 and at μ = 0.10 ($NaClO_4$), and at pH 13 (0.1 *N* NaOH) the TPPS again obeys Beer's law. (The concentration range of the study was $\sim 1 \times 10^{-4}$–1×10^{-9} *M*.) It is of of interest to note that a similar study on a trisulfonated TPP showed very large deviations from Beer's law in these concentration ranges.[5] This might be expected for the less sulfonated systems, where the hydrophobic phenyl group would like to get out of the water environment by associating with another unsulfonated phenyl group of another porphyrin, resulting in aggregation of the porphyrin species in solution. Thus the sulfonation of all four of the phenyl groups appears to be necessary for a well-behaved water-soluble porphyrin to exist.

When the TPPS is made acidic to form the porphyrin diacid, the behavior is very complicated; the interpretation of our observations is that in acidic regions (pH <2) the TPPS aggregates. Two

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[3] A. Triebs and N. Haverle, *Justus Liebigs Ann. Chem.*, **718**, 183 (1968); J. Winkelman, G. Slater, and J. Grossman, *Cancer Res.*, **27**, 2060 (1967); **22**, 589 (1962).

[4] A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, and T. Korsakoff, *J. Org. Chem.*, **32**, 476 (1967).

[5] R. F. Pasternack, private communication.

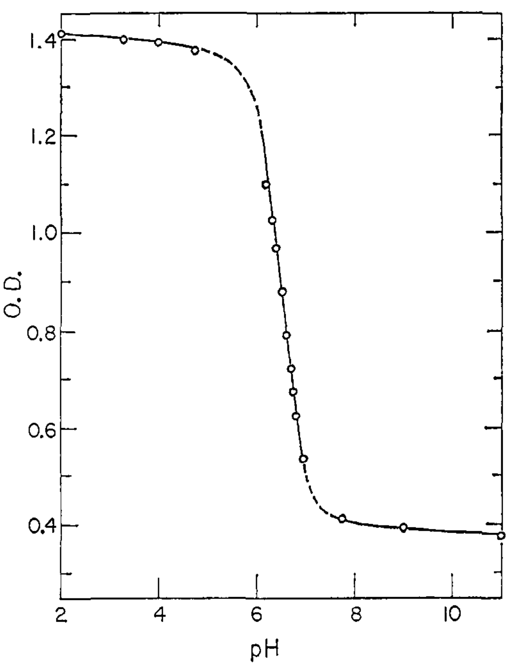

Figure 1. Spectrophotometric titration of $Fe^{III}TPPS$ at 11°

observations demonstrate this point. On making a neutral solution of TPPS acidic, the solution changes in color from orange to green. However, on standing there is a slow change of the diacid green species to another unidentified species with two new peaks at 489 and 708 nm. There is a complicated time dependence of the formation of this new "489-nm" species that is characterized by an induction period followed by a formation of the 489 nm peak; the induction period appears to be dependent on ionic strength. Because of the complicated behavior in the acid region we have not attempted either to make extensive measurements or to interpret the behavior in terms of particular molecular species in solution. It is known that the phenyl groups, which in the free base and metalloporphyrins are near to being perpendicular to the porphyrin ring, rotate toward the porphyrin plane in the diacid species.[1] This rotation would allow a closer interaction between two porphyrins and may account for the behavior observed in acidic solutions. If one carries out a spectrophotometric titration of TPPS very rapidly, one can get a qualitative idea of the TPPS pK. One obtains for the reaction

$$\text{TPPS} + H_n^{+} \overset{K_a}{\rightleftharpoons} \text{TPPS } H_n^{n+}$$

a p$K_a \sim 4.8$ and a value of $n = 2$ at an ionic strength of 0.10. These values are only approximate, though, because of the changes going on in solution in the acidic regions.

Sodium Tetra(*p*-sulfophenyl)porphineiron(III). Fe^{III}TPPS. A fourfold excess of $FeSO_4$ is added to a hot, neutral solution of Na_4TPPS which is obtained from the ammonium salt by treatment of that salt in solution with sodium methoxide. The use of the ammonium salt results in very poor yield of the iron complex. The red solution becomes yellow-brown almost immediately on the addition of the ferrous salt. The solution is heated on a steam bath for at least 30 min, at which time there is no longer any spectrophotometric evidence for the free-base porphyrin. Care must be taken to keep the pH of this solution above 6.0; the pH drops during the reaction and the metalation will not occur with the porphyrin in the diacid form. The solution is then cooled, acidified to pH 3, and passed through the H^+ form of the cation-exchange resin Dowex 50W-X8 (50–100 mesh) to remove the excess Fe^{3+}. As the solution passes through the resin it should immediately be neutralized, because acid solutions of the FeTPPS slowly degenerate to Fe^{3+} and the porphyrin diacid. Further purification (removal of Na_2SO_4) is accomplished by precipitation of the FeTPPS from a pH 5 solution by the addition of four volumes of acetone. The precipitate is redissolved in methanol and reprecipitated with acetone six times.

Anal. Calcd for $Na_3Fe^{III}TPPS \cdot 2H_2O$, $C_{44}H_{32}N_4S_4O_2Na_3$: C, 46.52; H, 2.47; N, 4.93. Found: C, 46.06; H, 2.48; N, 5.03.

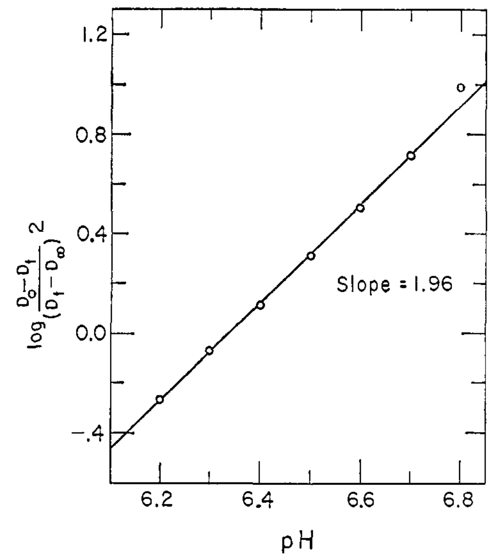

Figure 2. Analysis of spectrophotometric data of Figure 1.

Results

Monomer–Dimer Equilibrium. The structures of the monomer and dimer of the iron–tetraphenylporphine species have been definitively determined by X-ray diffraction.[6] The water-soluble tetra(*p*-sulfophenyl)-porphineiron complex [Fe^{III}TPPS] exists in a monomer form in acidic solutions and a dimeric form in basic solutions. The similarity of the visible absorption spectrum, infrared absorption spectrum, and magnetic properties of the sulfonated and nonsulfonated species attests to this fact, as seen by the data in the tables.

By carrying out a spectrophotometric titration of the Fe^{III}TPPS system the equilibrium constant and stoichiometry of the monomer–dimer reaction were determined.

$$2\text{FeTPPS} \overset{K_D}{\rightleftharpoons} \text{O-(FeTPPS)}_2 + 2H^+ \qquad (1)$$

$$K_D = [\text{O-(FeTPPS)}_2][H^+]^2/[\text{FeTPPS}]^2 \qquad (2)$$

Spectrophotometric titration of a solution of FeTPPS (1×10^{-4} M) with NaOH (in 0.1 M $NaNO_3$ to hold the ionic strength constant) shows two isosbestic points at 552 and 404 nm.

If D_0, D_∞, and D_+ are as defined in the Appendix, then it can be shown that a plot of log $[(D_0 - D_+)/(D_+ - D_\infty)^2]$ *vs.* pH should have a slope of 2 and an intercept of log K_D + log A (see eq 3). The study was carried out at three temperatures in a thermostated cell (11, 25, and 50°), using 528 nm to follow the reaction. The value of A at 25° and 528 nm, for example, is 1.95×10^{-4} [log $A = -3.71$]. The plots gave straight lines with slopes very close to the theoretical values of 2 (1.96, 1.97, and 1.98), demonstrating the correctness of the formulation given in eq 1. (See Figures 1 and 2.) Table I shows the results of these calculations including a $\Delta H°$ for the reaction which was determined by plotting log K_D *vs.* $1/T$.

$$\log\left[\frac{(D_0 - D_+)}{(D_+ - D_\infty)^2}\right] = \log K_D - n \log [H^+] + \log A \qquad (3)$$

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[6] E. B. Fleischer and T. S. Srivastava, *J. Amer. Chem. Soc.*, **91**, 2403 (1969); E. B. Fleischer, C. Miller, and L. Webb, *ibid.*, **86**, 2342 (1964).

Table I. Monomer–Dimer Equilibrium[a]

$$2\overset{\mathrm{OH_2}}{\mathrm{FeTPPS}} \xrightleftharpoons{K_D} \mathrm{O\text{-}(FeTPPS)_2} + 2\mathrm{H^+} + \mathrm{H_2O}$$

Temp, °C	K_D, M	Derived thermodynamic quantities,[b] kcal/mol
11	0.20×10^{-8}	$\Delta H° = 17.7 \pm 2.6$
25	0.79×10^{-8}	$\Delta G° = 11.1 \pm 0.5$
50	10.8×10^{-8}	$\Delta S° = 22.1 \pm 9.8$

[a] $\mu = 0.10$. [b] These values are not very accurate owing to the few data points taken to determine ΔH and ΔS. The estimated errors are based on possible systematic errors in the experiment and are not a measure of the precision of the experiment, which is much better than the errors indicated here.

The effect of the ionic strength on K_D is very large, as one would expect for the highly charged species of this system. K_D at 25° and $\mu = 0.10$ is 0.79×10^{-8}, while at the same temperature and $\mu = 1.0$, K_D was determined to be 0.3×10^{-6}. Thus we must be careful in comparing our results with those of other systems because of the large dependence of the properties of this system on ionic strength.

Kinetics of the Dimer–Monomer System. Decomposition of the Iron Dimer. The rate of the breakdown of the O-$(\mathrm{FeTPPS})_2$ dimer to the $\mathrm{Fe^{III}TPPS}$ monomer was followed with a Durham-Gibson stopped-flow spectrophotometer at 580 nm. Solutions of FeTPPS at pH 9.0 (2.0×10^{-4} M) were mixed with nitric acid solutions ranging from $[\mathrm{H^+}] = 1.1 \times 10^{-3}$ to 0.10 M. The ionic strength was maintained at $\mu = 0.10$ with $\mathrm{NaNO_3}$. The breakup of the dimer at constant ionic strength follows the rate law $-\mathrm{d[dimer]/d}t = \{k_{21} + k_{21}'[\mathrm{H^+}]\}[\mathrm{O\text{-}(FeTPPS)_2}]$, as shown by the plot in Figure 3 of the observed pseudo-first-order rate constants k_{obsd} *vs.* $[\mathrm{H^+}]$, with the resulting rate constants of $k_{21} = 41$ l./(mol sec) and $k_{21}' = 840$ M $\mathrm{sec^{-1}}$ at 25°.[7] The variation in k_{obsd} is ±3%.

Table II. Magnetic Susceptibility Data

Compound	Temp, °C	μ_{eff}[c,d]
FeTPPCl[a]	295	5.95
	195	5.89
	77	5.84
O-(FeTPP)$_2$[a]	294	1.85
	211	1.40
	194	1.27
	136	0.85
	77	0.68
MnTPPCl[a]	295	4.94
	195	4.90
	77	4.76
O-(MnTPP)$_2$[a]	295	4.12
	195	4.03
	77	3.93
FeTPPS[b]	313	5.90
O-(FeTPPS)$_2$[b,e]	313	3.02

[a] Faraday method in solid state. [b] Evans method in solution: D. F. Evans, *J. Chem. Soc.*, 2003 (1959). (The accuracy of this method is ~±1% for aqueous solutions.) [c] $\mu_{\mathrm{eff}} = 2.84\sqrt{T(\chi\,\mathrm{mol})}$. [d] Per gram atom of Fe(III). [e] pH 11.5.

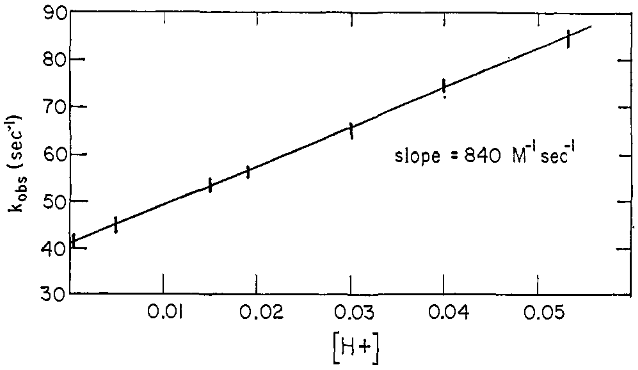

Figure 3. Plot of k_{obsd} *vs.* $[\mathrm{H^+}]$ for the reaction dimer → monomer.

Discussion

There can be no doubt that the water-soluble iron porphyrin FeTPPS exists as a μ-oxo dimeric species in solution at a pH greater than 9. The very similar spectroscopic properties of the O-$(\mathrm{FeTPPS})_2$ system and of the known Fe dimers as illustrated by the data in Tables II, III, and IV demonstrate this point. The O-$(\mathrm{FeTPP})_2$ has a five-coordinate Fe(III) atom in the crystalline state;[8] it is possible that in aqueous solution the O-$(\mathrm{FeTPPS})_2$ dimer is a six-coordinated species. The magnetic data shed some light on this question. The five-coordinate dimer, O-$(\mathrm{FeTPP})_2$, has a μ_{eff} at 25° of 1.85 BM. On the other hand, Cohen noted that when there was water of hydration in the iron dimer, the water presumed to be complexed, the magnetic moment was 2.68 BM at 25°. He found that as his sample was carefully dried the moment dropped to 1.74 BM. This implies that the presence of a water on the sixth coordination position increases the magnetic moment. The O-$(\mathrm{FeTPPS})_2$ dimer has a magnetic moment of 3.02 BM at 40° in aqueous solution. Thus the structure of the iron dimer of the sulfonated porphyrin in aqueous solution is most likely the six-coordinate species shown in Figure 4.

Table III. Infrared Spectra of Iron Metalloporphyrins in the Region 820–940 cm^{-1}

Compound	Absorption
FeTPPCl monomer	834 (w)[a]
O-(FeTPP)$_2$ dimer	878 (s) 892 (m)[a]
MnTPPCl monomer	833 (w)[a]
O-(MnTPP)$_2$ dimer	867 (s)[a]
FeTPPS monomer	850 (w)[b]
O-(FeTPPS)$_2$ dimer	872 (s)[b]

[a] Nujol. [b] KBr.

The magnetic properties of these systems have been studied in more detail by others;[9] it appears that in the iron dimer there exists an antiferromagnetic coupling of two ferric $S = {}^5/_2$ ions *via* the oxide bridge. This type

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[7] Dimer formation. A preliminary investigation showed that the kinetics of the dimer formation is second order in monomer with a decreasing rate as the pH is increased. The need for noninterfering buffers in the pH range of 7–9 has at the present time delayed a more complete and quantitative study of the formation reaction.

[8] I. A. Cohen, *J. Amer. Chem. Soc.*, **91**, 1980 (1969); E. B. Fleischer and T. S. Srivastava, *ibid.*, **91**, 2403 (1969).

[9] C. Maricondi and D. K. Straub, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, No. 55; A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961); W. M. Reif, G. J. Long, and W. A. Baker, Jr., *J. Amer. Chem. Soc.*, **90**, 6347 (1968); J. Lewis, F. Mabbs, and A. Richards, *J. Chem. Soc.*, 1014 (1967); S. Lippard, H. Schugar, and C. Walling, *Inorg. Chem.*, **6**, 1825 (1967); H. B. Gray, *Rec. Chem. Progr.*, **29**, 163 (1968), H. Schugar, C. Walling, R. Jones, and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3712 (1967).

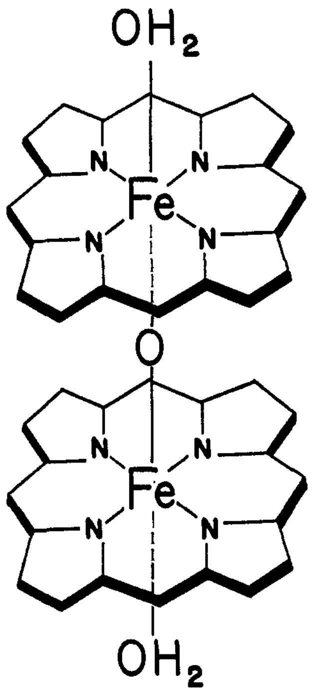


Figure 4. Schematic picture of O-$(FeTPPS)_2$ dimer; the sulfonated phenyls are left out of the figure for clarity.

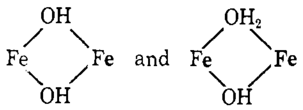
of system has been well characterized in the recent literature. It is quite interesting that a survey of the literature shows that most of the L-Fe(III)-O-Fe(III)-L systems have similar magnetic behavior which is quite independent of the ligands L of the system. The possibility in these types of systems of a dihydroxo-bridged dimer existing has been pointed out. The magnetic moment at room temperature of the dihydroxo bridged species would be expected to be about 5.1 BM.[10] This allows us to rule out the dihydroxo structure as a possibility since it has the much lower moment of 3.02 BM.

The kinetics of the breakdown of the O-$(FeTPPS)_2$ follows a rate law exhibited by other iron dimer systems.[11]

$$-\mathrm{d[dimer]}/\mathrm{d}t = (k_{21} + k_{21}'[\mathrm{H}^+])[\mathrm{Fe\ dimer}]$$

Some of the comparative rate data for this system are given in Table V. Comparisons made with these data should be made with the proviso that the studies and derived rate constants are for different ionic strengths.

All the cases studied have shown a hydrogen ion dependence of the dimer breakdown, although in the porphyrin case the k_{21}'/k_{21} is about 20, as compared to 10 for the aquo dimer and 10^6 for the other ligands. The detailed steps in the breakdown of the dimer are not known, but the mechanism probably involves addition of either an H_2O or H_3O^+ to the oxo-bridged dimer to form the intermediates



followed by the subsequent falling apart of these species to the monomer.[12]

Table IV. Visible Absorption Spectrum of Metalloporphyrins

Compound	Solvent	λ, nm	$\epsilon \times 10^{-4}$ M^{-1} cm^{-1}
FeTPPCl	$CHCl_3$	380	5.9
		417	11.0
		511	1.34
		577	0.33
		658	0.28
		690	0.32
O-$(FeTPP)_2$	Benzene	408	10.6
		571	1.07
		612	0.48
MnTPPCl	$CHCl_3$	378	5.6
		403	4.6
		480	10.9
		528	0.55
		538	0.54
		583	0.97
		618	1.06
FeTPPS monomer	H_2O^a	392	15.2
		528	1.4
		680	0.27
O-$(FeTPPS)_2$	H_2O^b	415	11.5
		565	0.88
		606	0.46
TPPS free-base form	H_2O^c	411	53.3
		515	1.6
		552	0.68
		580	0.64
		633	0.37
TPPS diacid form[e]	H_2O^d	434	44.2
		595	1.55
		644	4.60

[a] pH 3.3. [b] pH 11.2. [c] pH 10.0. [d] pH 3.8. [e] The pK_a of TPPS ($H_2TPPS + 2H^+ \rightleftharpoons H_4TPPS^{2+}$) is 4.8 (spectrophotometric titration, $\mu = 0.10$, $NaNO_3$). Below pH $\simeq 5.0$ ($\mu = 0.10$), a new species is observed with relatively intense peaks at 706 and 491 in addition to those of the diacid ($\epsilon \simeq 7 \times 10^4$ and 11×10^4, respectively; these values are dependent upon ionic strength). The rate and extent of formation of this presumably polymeric species are dependent upon ionic strength.

Table V. Kinetic Data on Breakdown of Iron Dimers (25°)

Ligand	k_{21}, sec^{-1}	k_{21}', M sec^{-1}	Ref
EDTA	1.2[c]	5.0×10^8	11
HEDTA	4.0[c]	3.0×10^6	11
H_2O	0.35[d]	3.5	*a*
TPPS	41[e]	840	*b*

[a] A. T. J. Conocchioli, E. J. Hamilton, and N. Sutin, *J. Amer. Chem. Soc.*, **87**, 926 (1965). [b] This work. [c] $\mu = 1.0$ ($NaNO_3$). [d] $\mu = 3.0$ ($NaClO_4$). [e] $\mu = 0.1$ ($NaNO_3$).

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Appendix. Equilibrium Constants from a Spectrophotometric Measurements of Reaction I

$$2\mathrm{A} \rightleftharpoons \mathrm{A}_2 + 2\mathrm{H}^+ \qquad \mathrm{(I)}$$

$$K_\mathrm{D} = \frac{[\mathrm{A}_2][\mathrm{H}^+]^2}{[\mathrm{A}]^2}, \quad \log K_\mathrm{D} = \log [\mathrm{A}_2]/[\mathrm{A}]^2 + 2 \log [\mathrm{H}^+]$$

If only the species A and A_2 absorb light in the region of interest (H^+ does not absorb), then we can derive the relations below. ϵ_1 and ϵ_2 are the extinction coefficients, c_1 and c_2 are the concentrations of the momomer A and dimer A_2 species, respectively, and D is the optical density. In the derivation we will assume a constant path length of 1.00 cm.

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$$c_{\text{tot}} = c_1 + 2c_2 = c_{10} = 2c_{2\infty}$$

$$D_+ = \epsilon_1 c_1 + \epsilon_2 c_2 \qquad D_0 = \epsilon_1 c_{10} \qquad D_\infty = \epsilon_2 c_{2\infty}$$

$$D_0 - D_+ = \epsilon_1 c_1 + 2\epsilon_1 c_2 - \epsilon_1 c_1 - \epsilon_2 c_2 = c_2(2\epsilon_1 - \epsilon_2)$$

$$D_+ - D_\infty = \epsilon_1 c_1 + \epsilon_2 c_2 - \epsilon_2 c_{2\infty} = \\ [(\epsilon_1 c_1 - \epsilon_2 c_2 - \epsilon_2 c_1)/2] - \epsilon_2 c_2 = c_1(\epsilon_1 - \epsilon_2/2)$$

$$\frac{D_0 - D_+}{(D_+ - D_\infty)^2} = \frac{2c_2[\epsilon_1 - \epsilon_2/2]}{c_1{}^2[\epsilon_1 - \epsilon_2/2]^2} = \frac{c_2}{c_1{}^2[\epsilon_1 - \epsilon_2/2]} \qquad (2)$$

Therefore,

$$\log\left[\frac{(D_0 - D_+)}{(D_+ - D_\infty)^2}\right] = \log K_D - 2\log[H^+] + \log A$$

and

$$A = 2/[\epsilon_1 - \epsilon_2/2]$$

If we define pH = $-\log[H^+]$, then a plot of $\log[(D_0 - D_+)/(D_+ - D_\infty)^2]$ *vs.* pH should be a straight line with slope 2 and intercept $\log K_D + \log A$. Since $\log A$ can be experimentally measured, the equilibrium constant K_D can be determined.

Metal Ion–Aromatic Complexes. XI. The Crystal and Molecular Structure of Bis(cyclohexylbenzene)silver(I) Perchlorate

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Abstract: The crystal and molecular structure of bis(cyclohexylbenzene)silver(I) perchlorate, $(C_6H_{11}C_6H_5)_2AgClO_4$, has been determined by single-crystal X-ray diffraction from 981 counter intensities measured at ambient room temperature. The crystals were found to be orthorhombic: $a = 32.17(2)$, $b = 5.666(3)$, $c = 12.67(1)$ Å; $Z = 4$; space group *Pmcn*. The structure was refined by full-matrix least squares to a final conventional *R* factor of 0.069. The crystal structure is composed of alternating layers of $AgClO_4$ and hydrocarbon which are of infinite extent in the *bc* plane. The molecular structure is described in terms of a "half-open hinge" with the connecting section removed and a silver ion displaced toward the open end of the hinge. The leaves of the "hinge" are the organic groups. The Ag(I) is three-coordinate with one donor bond from each of the two aromatic rings and the third interaction with an oxygen of the perchlorate group. The angular relationships between the three donors are such that it appears the silver is using either 5p or $5s5p^3$ orbitals as acceptors. The $AgClO_4$ chains propagate parallel to the *b* axis and are held together by weak Ag–O interactions and van der Waals forces. The silver–aromatic interaction is asymmetric, having Ag–C distances of 2.48 (1) and 2.66 (1) Å and Ag–C–C angles of 66 (1) and 82 (1)°.

Complexes formed between aromatic moieties and silver(I) were first described by Hill during the course of phase studies early in the 1920's,[2–4] but nearly 30 years elapsed before more significant work on these donor–acceptor complexes was reported. Both Mulliken[5] and Dewar[6] formulated theoretical models for the bonding in silver perchlorate–benzene, and the gross features of their models were verified by the crystal structures of $C_6H_6 \cdot AgClO_4$[7,8] and of $C_6H_6 \cdot AgAlCl_4$.[9] However, these structure results complicate the theoretical model that assumes a 1:1 interaction between the aromatic moiety and the silver ion. In the former case each silver ion is π bonded to two benzene rings such that a polymer, -Ar–Ag–Ar–Ag–, is formed, whereas in the latter case the silver ion is π bonded to only one benzene ring but interacts with four chlorine atoms to yield a five-coordinate Ag^+. There was extensive evidence from solution equilibrium studies of silver salts in aromatic–water systems, as reviewed by Andrews,[10] for the existence of complexes of the types $AgAr^+$ and Ag_2Ar^{2+}. Other solution work[11–16] indicated that stoichiometries other than one silver per aromatic were possible, but the first well-characterized crystalline complex of the type $AgAr_2^+$ was that of bis(cyclohexylbenzene)silver perchlorate, for which a preliminary communication has been published[17] and for which we wish to report here the synthetic and structural details.

The structures of two other complexes of the $AgAr_2^+$ type, bis(*m*-xylene)silver perchlorate[18] and bis(*o*-xylene)silver perchlorate[19] have now been published. More

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