negative peak observed at highest energy, the spectrum is exceedingly similar to those obtained with ASP, CYS, DABA, or ASG and is certainly not like those of the aliphatic amino acids. This result would indicate that the bonding interactions involve the ionized carboxylate and imidazole functional groups. Between pH 11 and 12, the CPL spectra decreased by approximately 50%, but were not observed to disappear completely. This observation indicates that the HIS ligand is only able to partially prevent the formation of the $[Tb(EDTA)]_x$ oligomers. In that case, the ternary formation constant of the Tb(EDTA)(HIS) complexes must be comparable to that of the $[Tb(EDTA)]_x$ oligomer, and this has been found to be the case (see Table I).

Conclusions

During the course of the present work, it has become established that amino acids may complex lanthanide ions by using many combinations of ligand functionalities. The formation of a chelate ring involving the α-amino carboxyl grouping is a relatively weak process but is certainly possible when metal ion solubility problems can be overcome. Other chelate ring systems can be formed (involving the ionized carboxylate and some other functionality) as long as the resulting ring is sufficiently small. These other ring systems are generally found to be considerably more robust than is the α-amino carboxyl ring system and will dominate the complexation chemistry whenever possible. When the formation of a chelate ring would require a large ring size, then complexation will take place solely at the α-amino carboxyl group and the additional functionality will play no role in the Tb(III) bonding.

It is quite clear from the present work that the solution-phase coordination chemistry of lanthanide complexes with amino acids is considerably more varied than hitherto suspected and certainly warrants further investigation.

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Effect of a Single Ortho Substituent on the Rate of Dimerization of Iron(III) Tetraphenylporphyrin Hydroxides

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The rates of conversion of iron(III) tetraphenylporphyrin hydroxides to the corresponding μ-oxo-bridged dimers have been studied for a series of porphyrins with a substituent attached by an ether linkage to the ortho position of one phenyl ring. The substituents were alkyl groups (ethyl and nonyl) and *tert*-butyl amides with one, two, or four CH_2 groups between the ether oxygen and the amide carbon. In these monosubstituted porphyrins the hydroxide ligand can be on the same side of the porphyrin plane as the ortho substituent (cis isomer) or on the opposite side of the plane (trans isomer). The rates of formation of the μ-oxo-bridged dimer in CCl_4 solution at room temperature were obtained by ^1H NMR. The data were consistent with a two-step mechanism. In the first step hydroxide dissociates from an iron porphyrin, either cis or trans. That porphyrin then reacts with a trans isomer to form the μ-oxo-bridged dimer. The rate of dissociation of hydroxide from the cis isomers was 7-70 times slower than from the trans isomers. As the number of CH_2 groups between the ether oxygen and the amide increased, the population of the cis isomer increased.

Introduction

In organic solvents many iron(III) porphyrin hydroxides (Fe-POH)[1] readily form μ-oxo-bridged dimers.[2] However, bulky substituents on iron(III) tetraphenylporphyrins inhibit dimerization and permit isolation of iron(III) porphyrin hydroxides.[3-11] One bulky ortho substituent on each side of the porphyrin plane was sufficient to prevent dimerization of an iron(III) porphyrin hydroxide.[12] We have recently shown that the rate of dimerization of FeTTPOH at room temperature in CCl_4 solution can be monitored by ^1H NMR.[13] The data were consistent with the two-step mechanism

$$\mathrm{FeTTPOH} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{FeTTP^+ + OH^-} \qquad (1)$$

$$\mathrm{FeTTP^+ + FeTTPOH} \xrightarrow{k_2} \mathrm{(FeTTP)_2O + H^+} \qquad (2)$$

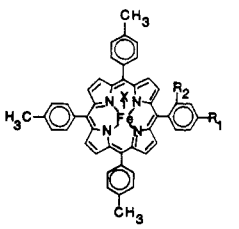
which gives the rate law

$$-\frac{\Delta[\mathrm{FeTTPOH}]}{\Delta t} = \frac{2k_1[\mathrm{FeTTPOH}]^2}{k'[\mathrm{OH^-}] + [\mathrm{FeTTPOH}]} \qquad (3)$$

where $k' = k_{-1}/k_2$ times the partition coefficient for the distribution of OH^- between water and CCl_4. For FeTTPOH $k_1 = (1.5 \pm 0.2) \times 10^{-4}$ s^{-1} and $k' = (0.2 \pm 0.15) \times 10^{-3}$.

In the preparation of a series of spin-labeled iron(III) tetraphenylporphyrins[14] it became evident that for some substituents on the ortho position of the phenyl ring a single substituent substantially decreased the rate of dimerization of the iron porphyrin hydroxide. We have therefore examined the rates of dimerization for five ortho-substituted porphyrins containing ether

Chart I



R_1	R_2	abbrev.
CH_3	H	Fe(TTP)X
H	OEt	Fe(TTP-OC_2)X
H	$O(CH_2)_8CH_3$	Fe(TTP-OC_9)X
H	$OCH_2\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}N$-t-Bu	Fe(TTP-OC_1A)X
H	$O(CH_2)_2\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}N$-t-Bu	Fe(TTP-OC_2A)X
H	$O(CH_2)_4\overset{\overset{H}{|}}{\underset{\underset{O}{\|}}{C}}N$-t-Bu	Fe(TTP-OC_4A)X

(1) Abbreviations used: P = porphyrin dianion; other abbreviations are defined by the structural formulas in Chart I.
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and amide linkages as shown below. Other authors have shown that ether and amide linkages on ortho-substituted tetraphenylporphyrins influence rates and equilibria for dioxygen binding to iron(II) porphyrins[15-17] and reduction potentials for iron(III) porphyrins.[18]

Experimental Section

Physical Measurements. Electronic spectra were obtained in chloroform solution on a Beckman Acta V spectrometer or on a Cary 14 with the On Line Instruments Systems modification. Spectra are reported below with wavelengths in nanometers and log ϵ given in parentheses. Infrared spectra were obtained on a Perkin-Elmer 283B spectrometer. NMR spectra were obtained in $CHCl_3$ or CCl_4 solutions on a Magnachem A200 FT NMR spectrometer at 22 °C. Chemical shifts are reported relative to tetramethylsilane (Me_4Si). Line widths for the paramagnetic complexes are reported in hertz. Kinetic studies were done in CCl_4. Spectra were collected with use of 8K data points and sufficient delay between pulses to give accurate integration of the signals.

Preparation of Porphyrins. 5-(2-Ethoxyphenyl)-10,15,20-tri-*p*-tolylporphyrin, H_2(TTP-OC_2). To a solution of 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin[19] (0.22 g, 0.33 mmol) in DMF (15 mL) was added excess anhydrous K_2CO_3 (0.7 g, 0.5 mmol) and excess ethyl iodide (0.86 g, 5.5 mmol). The reaction mixture was stirred at room temperature for 24 h, and then 20 mL of water was added. The porphyrin was collected by filtration and dried at 80 °C for 1 h. The product was chromatographed on alumina in $CHCl_3$. The rapidly moving first band was collected. The porphyrin was recrystallized from CH_2Cl_2/hexane; yield 0.20 g, 87%. IR: 3320 (NH) cm^{-1}. Vis: 648 (3.77), 591 (3.80), 551 (3.99), 517 (4.32), 420 (5.69), 403 sh (4.94). NMR ($CDCl_3$): δ 0.64 (t, 3 H, CH_2CH_3), 2.67 (s, 9 H, *p*-CH_3), 3.91 (q, 2 H, CH_2CH_3), 7.35 (m, 2 H, *m*-H, *p*-H on ortho-substituted phenyl), 7.59 (d, 6 H, *m*-H on tolyl rings), 7.72 (m, 1 H, *m*-H on ortho-substituted phenyl), 7.96 (m, 1 H, *o*-H on ortho-substituted phenyl), 8.06 (m, 6 H, *o*-H on tolyl rings), 8.78 (AB quartet, 4 H, pyrrole H), 8.81 (s, 4 H, pyrrole H).

5-(2-(Nonyloxy)phenyl)-10,15,20-tri-*p*-tolylporphyrin, H_2(TTP-OC_9). The porphyrin was prepared from nonyl bromide and 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin[19] by the procedure used to prepare H_2(TTP-OC_2); yield 85%. IR: 3320 (NH) cm^{-1}. Vis: 649 (3.76), 592 (3.77), 551 (3.96), 517 (4.28), 420 (5.70), 403 sh (4.96). NMR ($CDCl_3$): δ 0.40–0.90 (m, 17 H, $(CH_2)_7CH_3$), 2.66 (s, 9 H, *p*-CH_3), 3.83 (t, 2 H, OCH_2), 7.30 (m, 2 H, *m*-H, *p*-H on ortho-substituted phenyl), 7.51 (d, 6 H, *m*-H on tolyl rings), 7.70 (m, 1 H, *m*-H on ortho-substituted phenyl), 7.97 (m, 1 H, *o*-H on ortho-substituted phenyl), 8.06 (m, 6 H, *o*-H on tolyl rings), 8.78 (AB quartet, 4 H, pyrrole H), 8.81 (s, 4 H, pyrrole H).

5-(2-Carbomethoxyphenyl)-10,15,20-tri-*p*-tolylporphyrin (I). To a solution of 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin[19] (0.175 g, 0.26 mmol) in DMF (15 mL) was added 120 mg of crushed KOH pellets. Bromoacetic acid (0.036 g, 0.26 mmol) in DMF (5 mL) was added dropwise to the solution (30 min). The solution was stirred for 30 h at room temperature. A 70-mL portion of water was added, and the reaction mixture was neutralized with 1 M HCl. Porphyrin was collected by filtration. The product was dissolved in $CHCl_3$ and chromatographed on silica gel. The product was eluted with $CHCl_3$–ethanol (95:5) and recrystallized from CH_2Cl_2; yield 0.12 g, 63%. IR: 1600 (CO), 3320 (NH) cm^{-1}. Vis: 647 (3.66), 590 (3.71), 551 (3.89), 517 (4.22), 420 (5.67), 402 sh (4.89). NMR ($CDCl_3$): δ −2.72 (s, 2 H, NH), 2.69 (s, 9 H, *p*-CH_3), 4.42 (s, 2 H, OCH_2), 7.55 (m, 6 H, *m*-H on tolyl rings), 8.08 (m, 6 H, *o*-H on tolyl rings), 8.77 (m, 4 H, pyrrole H), 8.84 (m, 4 H, pyrrole H).

5-(2-Carbethoxyphenyl)-10,15,20-tri-*p*-tolylporphyrin (II). The porphyrin was prepared from 3-bromopropionic acid and 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin[19] by the procedure described for I; yield 70%. IR: 1710 (CO), 3310 (NH) cm^{-1}. Vis: 647 (3.73), 591 (3.82), 552 (3.98), 517 (4.30), 420 (5.72), 402 sh (4.95). NMR ($CDCl_3$): δ 1.80 (t, 2 H, $-CH_2COOH$), 2.58 (s, 6 H, *p*-CH_3), 2.66 (s, 3 H, *p*-CH_3), 3.98 (t, 2 H, OCH_2), 7.34 (m, 2 H, *m*-H, *p*-H on ortho-substituted phenyl ring), 7.48 (m, 6 H, *m*-H on tolyl rings), 7.70 (m, 1 H, *m*-H on ortho-substituted phenyl ring), 7.97 (m, 1 H, *o*-H, on ortho-substituted phenyl ring), 8.03 (m, 6 H, *o*-H on tolyl rings), 8.75 (AB quartet, 4 H, pyrrole H), 8.81 (s, 4 H, pyrrole H).

Preparation of Iron Porphyrins. Iron(III) 5-(2-Ethoxyphenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride, Fe(TTP-OC_2)Cl. H_2(TTP-OC_2) (0.080 g, 0.114 mmol) was dissolved in glacial acetic acid (100 mL) under nitrogen. The solution was heated to 85 °C. Pyridine (1.5 mL) and $FeSO_4 \cdot 7H_2O$ (1.5 mL of saturated aqueous solution) were added. The solution was kept at 85 °C for 30 min, cooled, and diluted with 100 mL of H_2O. The iron porphyrin that precipitated was collected by filtration and washed with H_2O. The product was chromatographed on silica gel in $CHCl_3$–MeOH (98.5:1.5). After removal of the solvent, the product was dissolved in $CHCl_3$. The solution was shaken vigorously with 2 M aqueous HCl to ensure that chloride was coordinated to the porphyrin. The product was recrystallized from CH_2Cl_2/hexane; yield 0.081 g, 90%. Vis: 692 (3.57), 659 (3.54), 579 (3.62), 512 (4.19), 418 (5.06), 382 (4.81), 346 sh (4.61). NMR (CCl_4): δ −0.6 (200-Hz line width (lw), CH_2CH_3), 6.2 (35-Hz lw, 9 H, *p*-CH_3), 11.8, 12.4, 12.9, 14.2 (80-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-(Nonyloxy)phenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride, Fe(TTP-OC_9)Cl. The complex was prepared from H_2(TTP-OC_9) by the procedure described for Fe(TTP-OC_2)Cl; yield 90%. Vis: 692 (3.54), 655 (3.47), 578 (3.57), 512 (4.17), 418 (5.06), 381 (4.81), 352 sh (4.66), NMR (CCl_4): δ −0.4 to +0.2 (17 H, $(CH_2)_7CH_3$), 6.2 (35-Hz lw, 9 H, *p*-CH_3), 11.8, 12.4, 12.9, 14.2 (90-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-Carbomethoxyphenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride (III). The iron porphyrin was prepared from porphyrin I by the procedure used to prepare Fe(TTP-OC_2)Cl; yield 88%. IR: 1750 (CO), 3450 (OH) cm^{-1}. Vis: 691 (3.52), 658 (3.58), 578 (3.57), 511 (4.14), 418 (5.01), 381 (4.76), 350 sh (4.57). NMR ($CDCl_3$): δ 6.45 (30-Hz lw, 9 H, *p*-CH_3), 12.2, 12.8, 13.4, 14.3 (80-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-(((*tert*-Butylamino)carbonyl)methoxy)phenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride, Fe(TTP-OC_1A)Cl. Iron porphyrin III (0.082 g, 0.10 mmol) was dissolved in dry benzene (50 mL). Oxalyl chloride (1.13 g, 10 mmol) was added, and the solution was stirred at room temperature for 2 h. The benzene was removed under vacuum. The residue was dried under vacuum for 2 h and dissolved in dry THF (75 mL). *tert*-Butylamine (0.073 g, 1.0 mmol) was added and the solution was refluxed gently for 3 h. The solvent was removed under vacuum, and the product was chromatographed on silica gel in $CHCl_3$–MeOH (98.5:1.5). The eluant was shaken with 2 M HCl. The product was recrystallized from CH_2Cl_2–hexane; yield 0.050 g, 57%. IR: 1680 (CO), 3400 (NH) cm^{-1}. Vis: 691 (3.52), 657 (3.46), 577 (3.56), 510 (4.15), 418 (5.03), 380 (4.76), 353 sh (4.61). NMR (CCl_4): δ 6.0, 6.1 (35-Hz lw, 9 H, *p*-CH_3), 11.7, 12.8, 13.7 (95-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-Carbethoxyphenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride (IV). The iron porphyrin was prepared from porphyrin II by the procedure described for III; yield 87%. IR: 1720 (CO), 3400 (OH) cm^{-1}. Vis: 692 (3.51), 658 (3.44), 578 (3.54), 512 (4.14), 418 (5.01), 383 (4.76), 350 sh (4.54). NMR ($CDCl_3$): δ 5.7, 5.8 (30-Hz lw, 9 H, *p*-CH_3), 10.5 11.2, 12.4, 13.5 (90-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-(2-(((*tert*-Butylamino)carbonyl)ethoxy)phenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride, Fe(TTP-OC_2A)Cl. The amide was prepared from IV by the procedure used to prepare Fe(TTP-OC_1A)Cl from III; yield 61%. IR: 1680 (CO), 3400 (OH) cm^{-1}. Vis: 693 (3.44), 657 (3.41), 579 (3.55), 511 (4.11), 417 (4.98), 382 (4.76), 352 sh (4.59). NMR (CCl_4): δ 1.0 (2 H, CH_2CO), 6.4 (35-Hz lw, 9 H, *p*-CH_3), 12.0, 13.2, 13.5, 15.3 (100-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-(Butoxycarbonyl)phenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride (V). The iron porphyrin was prepared from 5-(2-(butoxycarbonyl)phenyl)-10,15,20-tri-*p*-tolylporphyrin[20] by the procedure re-

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Table I. ^{1}H NMR Spectra of FePOH and $(FeP)_2O$[a]

porphyrin	pyrrole H	*m*-H	*p*-CH_3
Fe(TTP-OC_2)OH		10.0, 10.8, 11.9[b]	4.9[c]
Fe(TTP-OC_9)OH		10.0, 10.8, 11.8[b]	4.9[c]
Fe(TTP-OC_1A)OH		9.9, 10.8, 11.6[b]	4.7[c]
Fe(TTP-OC_2A)OH		10.0, 10.8, 12.8[b]	5.0, 5.2[c]
Fe(TTP-OC_4A)OH		10.2, 11.1, 11.9[b]	5.1[d]
$(Fe(TTP\text{-}OC_2))_2O$	13.4[b]		2.8[e]
$(Fe(TTP\text{-}OC_9))_2O$	13.3[b]		2.8[e]
$(Fe(TTP\text{-}OC_1A))_2O$	13.3[b]		2.8[e]
$(Fe(TTP\text{-}OC_2A))_2O$	13.4[b]		2.8[e]
$(Fe(TTP\text{-}OC_4A))_2O$	13.4[b]		2.8[e]

[a] Positions of peaks used in the kinetic studies. Chemical shifts are in ppm from Me_4Si in CCl_4 solution at room temperature. [b] Line widths about 100 Hz. [c] Line widths about 45 Hz. [d] Line width greater than for *p*-CH_3 in related compounds suggests the presence of two overlapping signals. [e] Line width about 10 Hz.

ported for the preparation of III; yield 88%. IR: 1670 (CO), 3400 (NH) cm^{-1}. Vis: 693 (3.51), 657 (3.44), 579 (3.55), 511 (4.15), 418 (5.03), 383 (4.78), 352 sh (4.59). NMR ($CDCl_3$): δ 1.43 (50-Hz lw, 6 H, $(CH_2)_3CO$), 5.82 (30-Hz lw, 9 H, *p*-CH_3), 10.9, 11.3, 12.5, 13.2 (75-Hz lw, 8 H, *m*-H).

Iron(III) 5-(2-(4-((*tert*-Butylamino)carbonyl)butoxy)phenyl)-10,15,20-tri-*p*-tolylporphyrin Chloride, Fe(TTP-OC_4A)Cl. The amide was prepared from V by the procedure used to prepare Fe(TTP-OC_1A)Cl from III; yield 60%. IR: 1670 (CO), 3350 (NH) cm^{-1}. Vis: 696 (3.54), 657 (3.48), 578 (3.58), 511 (4.18), 418 (5.04), 384 (4.82), 350 sh (4.63). NMR (CCl_4): δ −0.4 (350-Hz lw, 6 H, $(CH_2)_3$), 6.4, 6.6 (35-Hz lw, 9 H, *p*-CH_3), 12.1, 13.2, 14.6 (90-Hz lw, 8 H, *m*-H).

Preparation of Solutions of FePOH. A solution of FePCl in 3 mL of CCl_4 was stirred vigorously with 3 mL of 2 M HCl for about 5 min to ensure that no μ-oxo dimer was present. The CCl_4 solution was transferred to a flask containing 3 mL of 2 M NaOH in distilled water and stirred vigorously for 5 min. The color change of the organic phase from brown to green indicated that the conversion from FePCl to FePOH was complete within a few minutes. The phases were separated, and NMR spectra were obtained on the CCl_4 solution. The starting time for the reaction was defined as the time when the solution turned green. Most of the data were obtained on solutions that were initially 3 mM in FePOH. A few experiments were done with initial concentrations of FePOH between 0.75 and 2.0 mM to determine the dependence of the rates on the initial concentration of FePOH. A few experiments were also done to check the dependence of the rates on the concentration of hydroxide in the aqueous phase. After formation of FePOH the aqueous base solution was diluted to 1.0 or 0.5 M and stirring was continued for 5 min to equilibrate the CCl_4 solution with the lower concentration of hydroxide. Qualitative checks on toluene and benzene solutions indicated that the rates of dimerization were not strongly solvent dependent.

Kinetic Studies. NMR spectra of the solutions of FePOH were recorded within 10–20 min after starting the reaction. Five to twelve spectra were recorded during the course of the reaction. Data acquisition required about 15 min. The midpoint of the data collection was defined as the time for the measurement. The relative concentrations of FePOH and $(FeP)_2O$ were determined by integration of (a) the methyl signals for the two compounds and (b) the meta protons in FePOH compared with the pyrrole protons in $(FeP)_2O$. The two values were in good agreement. The chemical shifts and line widths of the signals used in the kinetic studies are given in Table I. The concentration of FePOH was plotted as a function of time. A plot of concentration as a function of time was generated by a computer program based on the mechanism discussed below. The rate constants were adjusted to fit the calculated curves to the experimental data. The bases for the choices of the values of the parameters are discussed below.

Results and Discussion

The ortho-substituted porphyrins were prepared by reaction of 5-(2-hydroxyphenyl)-10,15,20-tri-*p*-tolylporphyrin with bromo compounds to form ether linkages. ^{1}H NMR spectra contained signals characteristic of the substituent. The unsymmetrical substitution of the phenyl rings caused splitting of the pyrrole resonances into an AB quartet for the four protons on the two pyrrole rings adjacent to the ortho-substituted phenyl ring and a singlet for the four protons on the two pyrrole rings further from the ortho-substituted phenyl ring. The iron complexes (FePCl) were prepared by reaction of the porphyrins with $FeSO_4$ in glacial acetic acid.[21] The ^{1}H NMR spectra of FePCl had characteristic

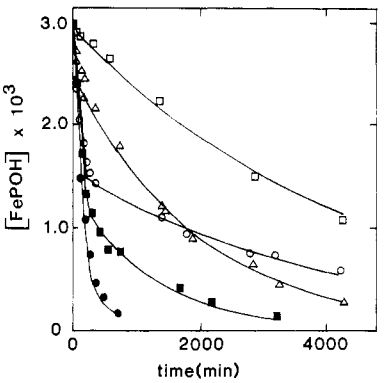

Figure 1. Changes in the concentration of FePOH as a function of time in CCl_4 solution at room temperature for P = TTP-OC_2 (●), TTP-OC_9 (■), TTP-OC_1A (○), TTP-OC_2A (△), and TTP-OC_4A (□). The solutions were prepared by shaking a 3 mM solution of FePCl with 2 M NaOH and separating the phases. The solid lines were calculated from the rate law given in eq 6 and the rate constants given in Table II.

signals at 6.4 ppm due to the *p*-CH_3 and three to four signals at 11.8–14.6 ppm due to the meta protons. In five-coordinate high-spin iron(III) porphyrins the meta protons are nonequivalent due to restricted rotation of the phenyl rings.[22] This causes splitting into two signals of equal intensity. In addition, in these mono-substituted complexes, the meta protons on the ortho-substituted ring had larger paramagnetic shifts than the meta protons on the tolyl rings.

We have recently shown that FeTTPOH can be prepared in situ by shaking a solution of FeTTPCl in CCl_4 with an aqueous solution of 2 M NaOH.[13] This procedure was used to prepare FePOH for the ortho-substituted porphyrins. The preparation of the hydroxide was confirmed by ^{1}H NMR and visible spectroscopy. The conversion of FePOH to $(FeP)_2O$ was monitored by ^{1}H NMR after separation of the phases. Plots of the concentration of FePOH as a function of time for the five iron porphyrins are shown in Figure 1. For each of the complexes there was a rapid initial phase of the reaction, followed by a slower phase. This biphasic behavior suggested that part of the FePOH reacted more rapidly than the remainder of the porphyrin. The slopes of the plots in the initial phase were similar to the slope of the plot for FeTTPOH. The concentration at which the rate change occurred and the slopes of the plots at longer times were strongly dependent on the ortho substituent.

For porphyrins with a single ortho substituent, the hydroxy group in FePOH can be on the same side of the porphyrin plane as the ortho substituent (cis isomer) or on the opposite side of the plane (trans isomer). These isomers could differ both in the rate of dissociation of hydroxide and in the equilibrium constants for hydroxide binding. However, in the dimer it seems probable that the ortho substituent would always be trans to the bridging oxygen. This suggests the following mechanism of formation of μ-oxo-bridged dimer

$$\begin{matrix} \textit{trans}\text{-FePOH} & \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & FeP^+ + OH^- \\ \textit{cis}\text{-FePOH} & \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} & \end{matrix} \qquad (4)$$

$$FeP^+ + \textit{trans}\text{-FePOH} \xrightarrow{k_2} (FeP)_2O + H^+ \qquad (5)$$

which gives the rate law

$$-\frac{\Delta[\text{FePOH}]}{\Delta t} = \frac{2(k_1[\textit{trans}\text{-FePOH}] + k_3[\textit{cis}\text{-FePOH}])[\textit{trans}\text{-FePOH}]}{k''[OH^-] + [\text{FePOH}]} \qquad (6)$$

(21) Smith, K. M., Ed. "Porphyrins and Metalloporphyrins"; Elsevier: New York, 1975; p 803.
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Table II. Rate Constants for Dimerization of FePOH[a]

porphyrin	% cis isomer[b]	k_1, s^{-1}	k''	k_3, s^{-1}
FeTTPOH		1.5×10^{-4} [c]	2×10^{-4} [c]	
Fe(TTP-OC_2)OH	50	1.7×10^{-4}	2×10^{-4}	2.5×10^{-5}
Fe(TTP-OC_9)OH	53	2.0×10^{-4}	2×10^{-4}	1.2×10^{-5}
Fe(TTP-OC_1A)OH	58	2.5×10^{-4}	2×10^{-4}	3.5×10^{-6}
Fe(TTP-OC_2A)OH	85	2.5×10^{-4}	2×10^{-4}	6.0×10^{-6}
Fe(TTP-OC_4A)OH	98	2.5×10^{-4}	2×10^{-4}	3.5×10^{-6}

[a] At 22 °C in CCl_4 solution. See text for definition of rate constants. [b] In the initial reaction mixture. [c] Values taken from ref 13.

where $k'' = (k_{-1} + k_{-3})/k_2$ times the partition coefficient for the distribution of OH^- between water and CCl_4.

In studies of the dimerization of FeTTPOH it was observed that if the initial concentration of FeTTPOH and the concentration of base in the aqueous phase were held constant, there was a family of solutions for k_1 and k' that gave comparable agreement with the experimental data. Unique values of the rate constants were obtained by varying the initial concentrations of iron porphyrin and base.[13] Since the rates of reaction of the substituted porphyrins in the initial rapid phase were similar to those observed for FeTTPOH and since several checks of the dependence of the rates on initial concentration of FePOH and on hydroxide concentration indicated that the dependence was similar to that observed for FeTTPOH, it was assumed that the values of k_1 and k' for the trans isomers of FePOH were similar to the values obtained for FeTTPOH. When the experimental data were fitted to the rate law (eq 6), only small variations in these parameters were examined. At long reaction times the calculated curves were relatively insensitive to the value of k''. For example, for Fe(TTP-OC_4A)OH a change in k'' by a factor of 10 caused only a 20% change in the value of k_3. Therefore, it was assumed that k'' was approximately equal to k'. The remaining adjustable parameters were k_3 and the populations of the cis and trans isomers. The slope of the plot at long reaction times was determined primarily by the value of k_3. The concentration at which the transition between the rapid and slow phases of the reaction was observed was determined by the populations of the cis and trans isomers and the value of k_3. The values of the rate constants used to obtain the calculated curves shown in Figure 1 are given in Table II. The variations in the values of k_1 may reflect the electronic effect of the ortho substituent.

The values of k_3 (Table II) were consistently smaller than the values of k_1, which indicated that the rate of hydroxide dissociation was slower for all of the cis isomers than for the trans isomers. The values of k_3 decreased in the order Fe(TTP-OC_2)OH > Fe(TTP-OC_9)OH > Fe(TTP-OC_2A)OH ≈ Fe(TTP-OC_1A)OH ≈ Fe(TTP-OC_4)OH. The biggest differences were between the trans and cis isomers and between the short ethoxy substituent and the substituents with longer chains. This pattern suggests that the size of the substituent may be an important factor in determining the value of k_3.

The population of the cis isomer (Table II) was also strongly dependent on the ortho substituent, but the pattern of substituent effects was quite different from that observed for the values of k_3. For Fe(TTP-OC_2)OH and Fe(TTP-OC_9)OH there was approximately equal population of the two isomers. Thus the long nonyl chain was not sufficient to favor the cis isomer. Only the substituents that included the amide linkages caused the cis isomer to be strongly favored. The population of the cis isomer increased as the number of CH_2 groups increased from one to two to four. Thus the amide group was necessary for stabilization of the cis isomer and the location of the amide relative to the hydroxide was also important. The differences in the trends for k_3 and the populations of the cis isomer suggest that the first is a general effect of a bulky substituent while the second is a specific effect of the amide group.

The populations of the isomers could be either kinetically or thermodynamically determined. The small values of k_1 and k_3 suggest that equilibrium would not be achieved during the brief time in which the FePOH was formed from FePCl and that the populations were kinetically determined. However, the possibility that faster processes could occur while the CCl_4 solutions were in contact with the aqueous base solutions cannot be ruled out. If the populations were kinetically determined, then the changes as a function of the ortho substituent indicate that the rate of formation of the cis isomer was substantially increased by the amide group. If the populations were thermodynamically determined, the changes indicate substantial stabilization of the cis isomer by the amide group.

Inspection of CPK molecular models indicated that the amide linkages could adopt conformations that put them in close proximity to the hydroxide in FePOH. If there were hydrogen bonding between the amide and OH^- in the reaction mixture, this might locate the hydroxide at a position that was favorable for reaction with the iron, thereby increasing the rate of formation of the cis isomer. Since the amide and the hydroxide are quite polar and the bulk CCl_4 solution is nonpolar, interaction in the FePOH complex between the two groups might contribute to a lower energy for the cis isomer. The models also indicated the possibility of hydrogen bonding between the axial ligand and the amide ligand, particularly for the longer substituent chains. If there were such an interaction, it would be expected to cause significant spin delocalization into the amide linkage and the adjacent atoms. The paramagnetic shifts for the meta protons on the substituted rings were consistently greater than for the unsubstituted rings but changed only slightly as the length of the ortho-substituent chain was varied. Thus the shifts of the meta protons more likely reflect the electron-donating effect of the ether group rather than the effects of spin delocalization through a hydrogen bond. The resonances for the *tert*-butyl groups were not observed for the FePOH or FePCl complexes, which indicated that the line widths for these signals were large. This could be due to dipolar broadening as a result of proximity to the iron or to spin delocalization. Thus it is difficult to argue either for or against the possibility of hydrogen bonding.

Comparison with Literature Results for Iron Porphyrins with Ether and Amide Linkages. The one example of a stable substituted iron(III) tetraphenylporphyrin hydroxide in which all the bulky substituents are on the same side of the porphyrin plane is a picket-fence porphyrin that has four amide linkages.[4] The μ-oxo-bridged dimer of the iron picket-fence porphyrin can be formed by reaction with Me_3NO,[4] which indicates that dimerization can occur if the oxygen is on the unhindered side of the porphyrin plane. The results obtained in this study suggest that the iron picket-fence porphyrin hydroxide is stable because it is formed predominantly as the cis isomer and that the amide linkages play an important, and previously unrecognized, role in stabilization of that isomer. If any of the hydroxide were formed as the trans isomer, it would probably convert to μ-oxo-bridged dimer quite readily.

The affinity of the iron(II) picket-fence porphyrin for O_2 and CO was found to be substantially greater than for other iron(II) tetraphenylporphyrin derivatives.[15] It has been suggested that the primary effect of the substituents on this reaction was via their influence on solvation. The substituents were viewed as disrupting solvation of the porphyrin plane, thereby diminishing the change in solvation that occurred upon binding the O_2 or CO.[15]

Iron(II) complexes of basket-handle porphyrins have also been found to have a high affinity for O_2.[16] The porphyrins with amide linkages caused a larger decrease in the rate of dissociation of the O_2 than the porphyrins with ether linkages. This was initially attributed to stabilization of the dioxygen by interaction with the polar amide groups.[16] A subsequent ^1H NMR study of the dioxygen adduct indicated the possibility of hydrogen-bonding interaction between the dioxygen and the amide NH.[17] In the iron(II) picket-fence porphyrin the distance between the amide N and the terminal O of the dioxygen was about 4 Å, which is longer than would be anticipated if there were hydrogen bonding. It was argued that the basket handle held the amide linkage closer to the metal than the preferred conformation for the individual pickets in the picket-fence porphyrin.

Electrochemical studies have also been done on the iron(III) porphyrin chlorides and hydroxides of the basket-handle porphyrins.[18] The substituents had large effects on the reduction potentials. The effect of the ether substituents was attributed to steric interference with solvation of the negatively charged species. The effects of the amide linkages were attributed to specific interactions involving either hydrogen-bonding or dipole–dipole interactions.

These literature results suggest that several factors contribute to the effects of ortho substituents on iron porphyrins. The relative importance of these factors varies from reaction to reaction. The factors that influence the rates of reaction of the iron porphyrin hydroxide may be quite different from those for oxygen binding because of the charge on the hydroxide ligand. Since the electrochemical studies were performed in polar solvents in the presence of high electrolyte concentrations, the solvation of the iron complexes is probably quite different from that in CCl_4 as used in the studies in this paper. Nonetheless, there is increasing evidence that both ether and amide substituents can have both general and specific effects on iron porphyrin reactions.

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Registry No. III, 98170-58-2; IV, 98170-59-3; V, 98170-60-6; Fe(TTP-OC_2)Cl, 98170-53-7; Fe(TTP-OC_9)Cl, 98170-54-8; Fe(TTP-OC_1A)Cl, 98170-55-9; Fe(TTP-OC_2A)Cl, 98170-56-0; Fe(TTP-OC_4A)Cl, 98170-57-1; Fe(TTP-OC_2)OH, 98170-61-7; Fe(TTP-OC_9)OH, 98170-62-8; Fe(TTP-OC_1A)OH, 98170-63-9; Fe(TTP-OC_2A)OH, 98170-64-0; Fe(TPP-OC_4A)OH, 98170-65-1.

Notes

Contribution from the Chemistry Department, University of Florence, 50132 Florence, Italy, and ISSECC (CNR), 50132 Florence, Italy

1,4,7,10,13,16,19-Heptaazacycloheneicosane. A Large, Potentially Dinucleating Polyazacycloalkane. Synthesis and Equilibria between Hydrogen and Copper(II) Ions

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Although there has been a considerable number of publications dealing with metal complexes of saturated polyazamacrocycles, relatively few studies are available on metal complexes of large polyazacycloalkanes (more than six nitrogens as donor atoms). These macrocycles are interesting mainly because they are potentially dinucleating ligands, able to incorporate more than one metal ion for each ligand molecule. In a previous paper[1] we have studied the coordination capabilities of the large polyazacycloalkane 1,4,7,10,13,16,19,22-octaazacyclotetracosane (bistrien). Continuing our studies on dinucleating polyazamacrocyclic ligands, we report here the synthesis of the large polyazacycloalkane 1,4,7,10,13,16,19-heptaazacycloheneicosane (L_1) and thermodynamic and electrochemical studies on its Cu(II) complexes.

Experimental Section

Synthesis of the Compounds. All chemicals were reagent grade and utilized without purification. Macrocycle L_1 has been synthesized by the general procedure (see Figure 1) of Atkins et al.[2] Experimental details of the synthetic procedure are reported in Table I. A dinuclear complex of formula $Cu_2(L_1)Cl(ClO_4)_3 \cdot H_2O$ can be isolated as a microcrystalline solid by mixing hot ethanolic solutions of copper(II) perchlorate and neutralized solutions of $(L_1) \cdot 7HCl$. (Anal. Calcd for $C_{14}H_{37}N_7O_{13}Cu_2Cl_4$: C, 21.54; H, 4.78; N, 12.56; Cl, 18.17. Found: C, 21.4; H, 4.9; N, 12.5; Cl, 18.1.) The magnetic moment of the complex measured by the Faraday method, is given by $\mu_{eff} = 2.81\ \mu_B$ at 298 K.

EMF Measurements. All potentiometric measurements were carried out in 0.5 mol dm^{-3} $NaClO_4$. The potentiometric titrations were carried out by using equipment (potentiometer, buret, stirrer, thermostated cell, microprocessor, etc.) that has been already described.[4] The computer program SUPERQUAD[5] was used to process data and calculate basicity and stability constants.

Electrochemical Measurements. Electrochemical analysis by cyclic voltammetry was performed with the following apparatus: a potentiostat (Amel Model 552), pen recorder (Amel Model 862/A) and a classical three-electrode cell. The working electrode was a platinum microsphere, the auxiliary electrode was a platinum disk, and the reference was an SCE electrode. Before each experiment the solution was carefully deoxygenated. Electronic spectra were recorded on a Varian Cary Model 17 spectrophotometer.

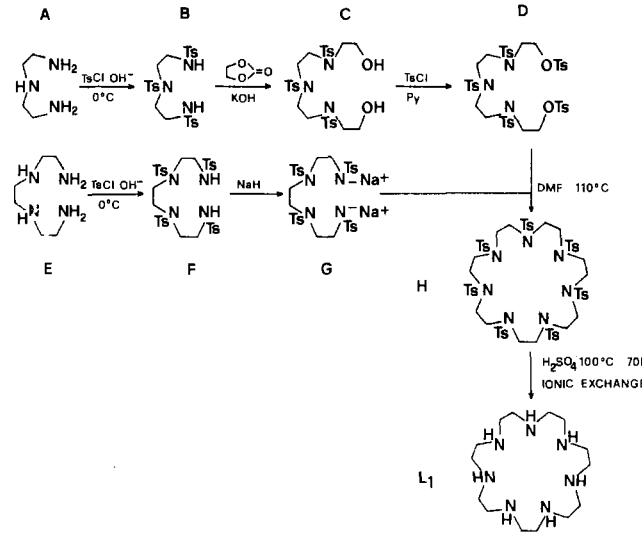

Figure 1. Reaction sequence for the synthesis of the macrocycle (L_1).

Results and Discussion

Protonation. The stepwise protonation constants for the macrocycle (L_1) are reported in Table II. For comparison, the protonation constants for the similar macrocycle bistrien are also reported. As already observed for polyazamacrocycles, values for the basicity constants constitute two groups.[1,4,6] The macrocycle (L_1) behaves as a strong base in the first three steps of protonation and as much weaker base in the last steps of protonation. Such a behavior can be easily rationalized in terms of electrostatic repulsion among the positive charges on the protonated cyclic polyamines.[6]

Copper(II) Complexes (Equilibrium Studies). Species and stability constants for the Cu(II) complexes with L_1 are reported

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