separations in the range of 2.4–2.6 Å.[4,8-10] In support of our claim that the phosphate ligands are fully deprotonated, we also find that each terminal oxygen has contacts to two sodium ions at distances ranging between 2.288 (2) and 2.765 (2) Å. Finally we should add that we cannot observe any electron density in the region of the terminal oxygens to indicate the presence of any hydrogen atoms, even though all the other hydrogen atoms in the structure were observed on difference maps.

The terminal guanine ligands are doubly deprotonated $C_5H_3N_5O^{2-}$ anions. As evidence for this claim, we find that the N9 hydrogen present in guanine monohydrate[11] is clearly missing, with N9 in this complex being coordinated to platinum in a planar fashion. The N1 hydrogen, also present in guanine monohydrate, is also missing. This is shown by the fact that no peak is apparent from difference maps, and also that N1 accepts a hydrogen bond from the water molecule O1W. The hydrogen atom involved in this contact is 1.90 (4) Å from N1, and is in the plane of the guanine ligand. The N–C distances involving N1, N1–C6 and N1–C2, have shortened from the values 1.398 and 1.371 Å in guanine monohydrate, to 1.347 (4) and 1.348 (4) Å in this complex anion. The corresponding change in the C2–N1–C6 angle is from 124.6 to 119.1 (2)°. No hydrogens are observed on N3 and N7 in our complex anion, and there are also no differences in the bond distances and angles about these atoms between this structure and that of guanine monohydrate. Furthermore, N3 has a close contact to Na^+ (N3···Na1 = 2.453 (2) Å), N7 has contacts to two Na^+ ions (N7···Na3 = 2.499 (3) Å; N7···Na4 = 2.951 (3) Å, and the carbonyl oxygen O9 has two close contacts to Na^+ (O9···Na3 = 2.604 (2) Å; O9···Na4 = 2.520 (3) Å). This formulation corresponds to a decanegative anionic complex with two platinum(III) centers.

Since the μ-phosphato bridges are fully deprotonated, the only plausible interligand H-bonding is between the hydrogens on N2 and one of the terminal phosphato oxygens.[12] It is clear from the long internuclear separations between N2 and O5, O6, O7, and O8 that there are no interligand H-bonds within this structure.

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Registry No. $Na_{10}[Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2]\cdot xH_2O$, 103883-58-5; Pt, 7440-06-4.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen atom coordinates and isotropic thermal parameters, and least-squares planes (4 pages); table of observed vs. calculated structure factors for $Na_{10}[Pt_2(\mu\text{-}PO_4)_4(C_5H_3N_5O)_2]\cdot 22H_2O$ (25 pages). Ordering information is given on any current masthead page.

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Characterization of Iron(III) Porphyrins Bearing Aliphatic Amine Ligands

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The facile autoreduction of Fe(III) porphyrins by electron-rich ligands has been known for many years. Ligands such as aliphatic amines,[1-4] cyanide,[3,5] thiols,[6] imidazolates,[7] pyridine/hydroxide[1b,8] and alcoholates[8b,9] all reduce the Fe(III) complex to its Fe(II) oxidation state. In fact, autoreduction has been used to prepare Fe(II) species for investigation by Mössbauer,[1] X-ray,[2] flash photolysis,[4] and electron-transfer[5] techniques. In many other instances, however, autoreduction precludes study of a desired Fe(III) species. In particular, aliphatic amines generally induce rapid and complete autoreduction and it is generally supposed that Fe(III) porphyrin–aliphatic amine complexes cannot be formed. We are aware of only two counterexamples: the tetraphenylporphyrin derivatives $Fe^{III}TPP(pip)_2Cl$[3c] and $(T(2,4,6\text{-}EtO)_3PP)Fe^{III}(pip)_2Cl$.[10] These were observed by ^1H NMR in CD_2Cl_2 (−78 °C) and $CDCl_3$ (room temperature), respectively; autoreduction is usually very slow in these solvents.[3] In this paper we report that aliphatic amines bind to ferric porphyrins in the presence of cyanide to give Fe^{III}(porphyrin)(RR'NH)(CN^-) complexes. At low ligand concentration under air, these species remain for days even in Me_2SO, a solvent in which autoreduction is generally very rapid.[3]

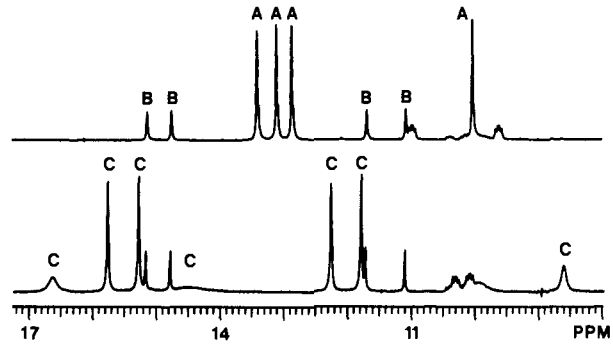

Figure 1. Fe^{III}PPIXDME in Me_2SO-d_6: upper, 1 equiv of CN^-; lower, 1 equiv of CN^- and 4 equiv of n-$BuNH_2$; (A) monocyano complex; (B) dicyano complex; (C) CN^-, n-$BuNH_2$ complex.

When aliphatic amines are added to an NMR tube containing a ferric porphyrin and 1 equiv of cyanide in Me_2SO-d_6, a new species grows in. In the case of iron(III) protoporphyrin IX dimethyl ester (Fe^{III}PPIXDME) and n-$BuNH_2$, this species had a new set of resonances corresponding to the hemin ring protons as well as four new peaks corresponding to the resonances of the bound n-$BuNH_2$, as seen in Figure 1. Integration showed that only one butylamine was bound. Different species, with much broader line widths, were formed in the absence of cyanide, indicating that cyanide rather than Me_2SO was the sixth ligand.

The chemical shifts of the axial butyl group were at 14.4, 16.6, 8.6, and 3.8 ppm down the chain with line widths of 173, 44, 27, and 15 Hz, respectively. The assignment of the β, γ, and δ

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Table I. Chemical Shifts of Primary Aliphatic Amines Bound to Ferric Porphyrins [$Fe^{III}Por(RNH_2)(CN^-)$][a]

RNH_2 ligand	α	β	γ	δ
	Fe^{III}PPIXDME			
n-$PrNH_2$	*b*	17.5	7.75	
n-$BuNH_2$	14.4	16.6	8.6	3.8
$(CH_3)_2CHCH_2NH_2$	14.6	17.8	8.6	
$(CH_3)_3CCH_2NH_2$	*b*		7.6	
$(CH_3)_2NCH_2CH_2NH_2$	16.1	17.8		7.3
$(n\text{-}BuNH_2)_2$	18.7	23.8	13.2	5.8
	(4-MeTPP)Fe^{III}			
n-$BuNH_2$	14.0	16.2	8.0	*b*
$(CH_3)_2CHCH_2NH_2$	13.9	16.3	8.2	
$(CH_3)_3CCH_2NH_2$	14.8		9.3	

[a] In Me_2SO-d_6 at room temperature. [b] Not observed.

resonances were made by observing cross peaks in the 2D COSY spectrum. The cross peak between the α- and β-CH_2 protons was not seen, presumably because the α-CH_2 resonance relaxed too quickly. The α-proton resonances were assigned by comparing the integrated areas of the propyl-, isopropyl-, isobutyl-, and neopentylamine complexes. The chemical shifts of the corresponding n-butylamine complex of (4-MeTPP)Fe^{III} were similar to those of the protohemin with three of the butylamine resonances observed at 14.0, 16.2, and 8.0 ppm (the fourth presumably under resonance of the hemin). Under conditions that gave a majority of the RNH_2, CN^- complex (1 equiv of CN^- and 4 equiv of RNH_2 in Me_2SO-d_6 at room temperature), the more hindered secondary amine $CH_3NH(CH_2)_3CH_3$ bound only poorly to Fe^{III}PPIXDME(CN^-). The tertiary amine $(CH_3)_2N(CH_2)_3N(CH_3)_2$ and *tert*-butylamine did not bind. Chemical shifts of the various complexes are given in Table I.

Titration studies were run to determine the relative ligand-binding affinities of the cyanohemin for aliphatic amine and 1-MeIm. A solution of Fe^{III}PPIXDME with 1 equiv of cyanide (80:20 ratio monocyano to biscyano)[11] was titrated with n-$BuNH_2$. Peaks due to the n-$BuNH_2$, CN^- complex grew in largely at the expense of the monocyano complex. Addition of 1.5 equiv of n-$BuNH_2$ gave a mixture of all three species; addition of 2.5 equiv of n-$BuNH_2$ gave n-$BuNH_2$, CN^- and dicyano complexes in about an 80:20 ratio. Addition of 1 equiv of 1-MeIm gave a mixture of three species: 1-MeIm, CN^- (40%), n-$BuNH_2$, CN^- (45%), and CN^-, CN^- (15%). At 4 equiv of 1-MeIm the complexes were found in a 65:20:15 ratio. The reverse titration was run (i.e. addition of the ligands in the order CN^-, 1-MeIm, n-$BuNH_2$), and the results were very similar. These titrations indicate that the equilibrium constants for forming the 1-MeIm, CN^- and n-$BuNH_2$, CN^- complexes are approximately equal in Me_2SO. Cyanide has a higher affinity than n-$BuNH_2$ for the Fe^{III}PPIXDME(CN^-) complex, as shown by the addition of a second equivalent of CN^- to a solution containing 1 equiv of CN^- and 20 equiv of n-$BuNH_2$; only the dicyano complex was seen.

The ratios of the species were similar but not identical from run to run. In addition, the relative ratios of the species would usually change somewhat upon standing overnight. These observations may be due in part to the slow off rate for CN^- from the dicyano complex.[5] Also, the excess of ligand over hemin is small in these titrations and traces of acid can protonate both CN^- and n-$BuNH_2$.

Two aminoimidazoles were investigated, the (aminopropyl)-imidazole 1-[$H_2N(CH_2)_3$]Im[12] and homohistamine, 5-[H_2N-$(CH_2)_3$]Im.[13] When a mixture of the monocyano and dicyano Fe^{III}PPIXDME species was titrated with the former compound, complex spectra were seen, appropriate for a mixture in which complexes with the imidazole nitrogen bound and complexes with the amino nitrogen bound were both present in solution. However, when homohistamine was used as the titrant, only one major new species was seen. This species contained only one imidazole, as indicated by integration of the ring methyl resonances vs. a new peak at 12.7 ppm. This peak is presumably the CH_2 protons α to the imidazole ring; the methyl resonance of the 5-MeIm, CN^- complex is found at 12.9 ppm.

Binding at only the imidazole nitrogen in this complex is presumably due to intramolecular hydrogen bonding in the homohistamine. It is not known whether the important aspect of this intramolecular hydrogen bonding is to reduce the availability of the amine lone pairs or make the imidazole nitrogen a better ligand. Valentine and co-workers have observed intramolecular hydrogen bonding in complexes Fe(TPP)$(L)_2SbF_6$ where L is *cis*-methyl urocanate (imidazole intramolecularly hydrogen-bonded to an ester carbonyl in a 7-membered ring).[14]

When 4 equiv of n-$BuNH_2$ were added to Fe^{III}PPIXDME in Me_2SO at room temperature, a species appeared with a peak at 19.7 ppm (4 H). However, the lines were broad, due either to ligand exchange or to autoreduction and electron exchange on the NMR time scale. The bis(butylamine) complex was readily formed with 4 equiv of n-$BuNH_2$ in $CDCl_3$ at −18 °C. By analogy with the monoamino, monocyano complexes, the resonances were assigned in order down the chain at 18.7, 23.8, 13.2, and 5.8 ppm (COSY cross peak seen only between γ- and δ-CH_2).

The monoamino, monocyano species described in this work are stable for days in Me_2SO in the air. Even when a tube with a solution of Fe^{III}PPIXDME and 1 equiv of CN^-, 1.5 equiv of 1-MeIm, and 3 equiv of n-$BuNH_2$ (65% 1-MeIm, CN^-, 25% n-$BuNH_2$, CN^-, and 10% CN^-, CN^-) was purged with Ar for 10 min, no autoreduction was seen after 4 days. The major reason for the stability of the complexes reported in this work is probably that the ligand concentration is very low (1 equiv of ligand $\simeq$ 10 mM in these experiments). La Mar and del Gaudio have shown that the rate of autoreduction increases with increasing ligand concentration for both the bis(piperidine) and dicyano complexes of Fe^{III}TPP.[3]

We have shown that ferric porphyrins bearing axial aliphatic amine ligands can be quite stable. This will allow study of many other characteristics of these species. These complexes are also models for heme protein states in which a lysine is thought to be bound to the iron.[15] The methylenes α and β to the amine of the lysine should have chemical shifts that place them outside of the protein envelope.

Experimental Section

Ferric protoporphyrin IX dimethyl ester (Fe^{III}PPIXDME(Cl)) was prepared from iron(III) protoporphyrin IX chloride (Midcentury) by following the mixed-anhydride method of Traylor et al.[16] Ferric tetrakis(4-methylphenyl)porphyrin chloride, (4-MeTPP)Fe^{III}Cl, was obtained from Midcentury Chemicals and used as received. n-Propylamine, n-butylamine, isobutylamine, *tert*-butylamine, neopentylamine, N-methylbutylamine, N,N-dimethylethylenediamine, N,N,N',N'-tetramethylpropanediamine, and 1-methylimidazole were obtained from Aldrich and used as received. 1-(3-Aminopropyl)imidazole, 1-[H_2N-$(CH_2)_3$]Im, was synthesized by the method of Schwan.[12] Homohistamine, 5-[$H_2N(CH_2)_3$]Im, was synthesized by the method of Black and Parson.[13] Proton NMR spectra were recorded at room temperature with use of a 5-mm probe on a Varian XL-300 spectrometer operating at 299.943 MHz.

For the titration experiments, Fe^{III}PPIXDME(Cl) or (4-MeTPP)-Fe^{III}Cl (3.5 mg, $\sim 5.2 \times 10^{-3}$ mmol) was dissolved in 0.40 mL of Me_2SO-d_6 (99.5 atom %, MSD Isotopes) in an NMR tube. Potassium cyanide (1 equiv, 2.5 μL of a 2.0 M solution in D_2O) was added. No attempt was made to exclude oxygen. The resulting solution was titrated with the appropriate amine.

Acknowledgment. We thank the National Institutes of Health for support of this work (Grant AM30479). The Varian XL-300

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spectrometer was funded through NIH Grant 1 S10 RR02004 and a gift from the Monsanto Co.

Registry No. Fe(PPIXDME)(CN), 59890-73-2; Fe(PPIXDME)-$(CN)_2^-$, 64060-98-6; Fe(PPIXDME)(CN)(*n*-$BuNH_2$), 103836-00-6; Fe(PPIXDME)(CN)($PrNH_2$), 103836-01-7; Fe(PPIXDME)(CN)(*i*-$PrNH_2$), 103836-02-8; Fe(PPIXDME)(CN)(*i*-$BuNH_2$), 103836-03-9; Fe(PPIXDME)(CN)(*neo*-$C_5H_{11}NH_2$), 103836-04-0; Fe(4-MeTPP)-(CN)(*n*-$BuNH_2$), 103836-05-1; Fe(PPIXDME)(CN)(CH_3NH-$(CH_2)_3CH_3$), 103836-06-2; Fe(PPIXDME)(CN)(1-MeIm), 100473-40-3; Fe(PPIXDME)(CN)(1-[$H_2N(CH_2)_3$]Im) (isomer 1), 103836-07-3; Fe(PPIXDME)(CN)(1-[$H_2N(CH_2)_3$]Im) (isomer 2), 103836-08-4; Fe-(PPIXDME)(CN)(5-[$H_2N(CH_2)_3$]Im), 103836-09-5; Fe-(PPIXDME)(CN)(5-MeIm), 103836-10-8; Fe(PPIXDME)(*n*-$BuNH_2)_2^+$, 103836-11-9.

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Synthesis and Characterization of a *meso*-Tetrakis(4-ferrocenylphenyl)porphyrin and Examination of Its Ability To Undergo Intramolecular Photocatalyzed Electron Transfer

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Modeling of the light-initiated electron transfer in photosynthesis has received much attention in recent years.[1] A system that has been widely used is a porphyrin with a covalently linked quinone.[2] Upon excitation of the porphyrin to its singlet excited state, an electron can be transferred to the quinone moiety, forming a quinone anion radical and a porphyrin π-cation radical. This high-energy ion pair collapses in a nano- or picosecond time scale to the neutral species.[3] We were interested in a model system where, upon photoinduced electron transfer, a more stable species results. A promising candidate seemed to be a porphyrin with linked ferricenium ions. Electron transfer to the ferricenium ion should quench the porphyrin fluorescence.

In this paper we wish to report the synthesis of a ferrocene-substituted porphyrin, its electrochemistry, and oxidation to the porphyrin ferricenium cation. Also, the fluorescence and phosphorescence of the porphyrin ferricenium compound is investigated. We choose to study *meso*-tetrakis(4-ferrocenylphenyl)porphyrin (**1**). In **1** the phenyl substituents are out of plane with the porphyrin ring so that they serve only as spacer groups allowing rotational freedom to the ferricenium while providing for a rather rigid system with a fixed distance between the donor and the acceptor groups. The center to center distance of 10.4 Å, as calculated from published crystallographic data on *meso*-tetraphenylporphyrin[4] and ferrocene,[5] is ideal for electron transfer.[6]

meso-Tetrakis(4-ferrocenylphenyl)porphyrin (**1**) was prepared from 4-ferrocenylbenzaldehyde[7] and pyrrole in 15% yield according to the method of Adler et al.[8] The isolation of **1** was complicated by its low solubility. It is insoluble in almost any solvent except chlorinated aromatic solvents, in which it is slightly soluble. Approximation 10^{-5} M solutions can be obtained in *o*-dichlorobenzene at 25 °C. Protonation at the pyrrole nitrogen atoms made porphyrin **1** fairly soluble in polar solvents. This enabled us to obtain a ^1H NMR spectrum of the diprotonated form in deuteriochloroform/deuteriotrifluoroacetic acid. The structure of product **1** was established beyond doubt by UV-vis spectroscopy, laser desorption Fourier transform mass spectroscopy,[9] and elemental analysis. Contrary to the case of *meso*-tetraferrocenylporphyrin,[10] **1** showed a UV-vis spectrum (see Experimental Section) almost identical with that of *meso*-tetraphenylporphyrin,[11] which indicates that there is little or no electronic interaction between the porphyrin and the ferrocene π-system.

(*meso*-Tetrakis(4-ferrocenylphenyl)porphinato)zinc (**2**), which was prepared from **1** and zinc acetate[4] in 67% yield, was even less soluble than the free-base species.

The thin-layer cyclic voltammogram of **1** in a 1:1 mixture of *o*-dichlorobenzene and acetonitrile gave an oxidation wave at +0.64 V and a reduction wave at +0.54 V, both of which by

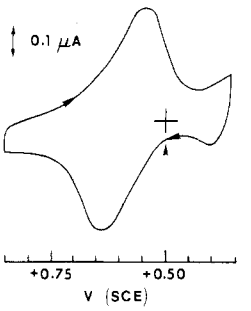
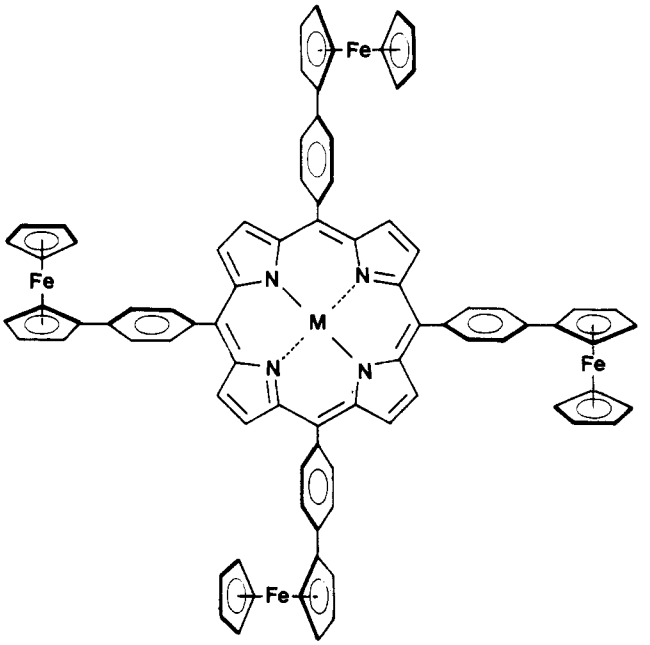


Figure 1. Thin-layer cyclic voltammgram of **1** (1.5×10^{-5} M) in a 1:1 *o*-dichlorobenzene/acetonitrile solution (0.1 M TBAP). Coulometry by integration of the area under the peak heights, after substraction for solvent contribution, indicates that 4 electrons are involved in both anodic and cathodic sweeps. The midpoint potential is at +0.59 V (SCE).



1, M = H_2
2, M = Zn

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