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Supplementary Material Available: Infrared spectra of theophylline and $(\eta^5\text{-C}_5\text{H}_5)_2(\text{C}_7\text{H}_7\text{N}_4\text{O}_2)\text{Ti}^{\text{III}}$ (Figure 4), listings of refined temperature factors (Table IV), distances and angles involving the hydrogen atoms (Table V), and weighted least-squares planes (Table VI), and a survey of interatomic distances and bond angles in crystal structures of theophylline derivatives (Table VII) (16 pages). Ordering information is given on any current masthead page.

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Electrochemistry of Nitrite Reductase Model Compounds. 2. Formation of an Iron Bis-Nitro Porphyrin Complex

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The reaction of $\text{Fe}^{\text{III}}(\text{P})\text{Cl}$ and $\text{Fe}^{\text{III}}(\text{P})(\text{NO}_2)$ (where P = tetraphenylporphyrin (TPP), tetraphenylchlorin (TPC), and octaethylporphyrin (OEP)) with nitrite was studied by UV/visible, proton NMR, and infrared spectroscopy and by electrochemistry. Quantitative analysis of the visible spectra generated by the titration of ferric-porphyrin complexes with nitrite showed the appearance of mono- and bis-nitrite complexes. The red shift of the Soret band for the bis-nitrite complexes of $\text{Fe}^{\text{III}}\text{TPP}$ and -TPC is consistent with an anionic porphyrin complex. If a stronger axial ligand such as chloride was present, it was difficult to observe the mono-nitrite intermediate. Proton NMR of the titration of $\text{Fe}(\text{TPP})(\text{NO}_2)$ with nitrite in DMF showed that both the mono and bis complexes were low spin, while the infrared spectrum was consistent with a Fe-N-bonded nitro complex. The cyclic voltammograms at slow scan rates of $\text{Fe}(\text{TPP})(\text{NO}_2)$ in DMF and Me_2SO in the presence of nitrite showed reversible waves, and the shift in the $E_{1/2}$ values was consistent with the formation of mono- and bis-nitro complexes, with no coordination of the ferrous complex with nitrite. The formation constants calculated voltammetrically were consistent with the spectroscopically obtained values. The presence of the mono- and bis-nitro complexes was also seen for high concentrations of nitrite (about 20 mM) where, at high scan rates, a second reduction wave, which grew at the expense of the wave seen at low scan rates, was observed to be about 150 mV more negative than the original ferric/ferrous wave. Thus, the reduction must proceed by dissociation of the bis-nitrite complex to the mono-nitrite complex prior to reduction. At high scan rates, the dissociation of the bis-nitrite complex is too slow for the reduction to proceed exclusively through that mechanism, and a new wave is seen for the direct reduction of the bis-nitrite complex. A single oxidation wave was observed at all scan rates. For $\text{Fe}(\text{OEP})(\text{NO}_2)$, there is evidence that one of the nitrite ligands remains coordinated in the ferrous oxidation state. In methylene chloride, the ferric/ferrous wave was irreversible, and the details of the electrochemistry are still under investigation. For all porphyrins and solvents studied, a new wave was seen at about -0.9 V vs. Ag/AgCl when nitrite was present. At this potential, one expects either NO or $\text{Fe}(\text{L})(\text{NO})$ to reduce. At this time, the evidence points to the origin of this wave being due to NO and not $\text{Fe}(\text{L})(\text{NO})$ when the solvent is DMF. During prolonged electrolysis, as in coulometry, though, a significant amount of $\text{Fe}(\text{L})(\text{NO})$ was eventually formed.

Introduction

The enzymatic reduction of nitrite to ammonia (assimilatory nitrite reduction) is catalyzed by a class of enzymes with the same prosthetic groups: one siroheme (an iron isobacteriochlorin)^{1,2} and an Fe_4S_4 cluster.^{3,4} While the details of the enzymatic reduction have not been elucidated yet, work thus far has shown that nitrite reacts with the siroheme to form a nitrite complex that is reduced to an iron nitrosyl,⁵ hydroxylamine, and then ammonia.² There is a second class of enzymes, the dissimilatory nitrite reductases, that reduce nitrite to nitric oxide, nitrous oxide, or dinitrogen. This enzyme contains two hemes *c* and two hemes *d*₁. For heme *d*₁, both a chlorin^{6,7} structure and a dioxoisobacteriochlorin⁸ structure have been proposed. As with the assimilatory enzymes, a nitrite complex is formed⁹ that is reduced to nitric oxide,^{10,11} nitrous oxide, or dinitrogen. The exact structure of the nitric oxide intermediate is still unclear and recent work has shown that labeled nitric oxide will not reduce to nitrous oxide, while labeled nitrite will.^{12,13} An "HNO" species is thought to be involved.

The importance of the chlorin and isobacteriochlorin groups in the functioning of the enzymes is still an open question. The electrochemistry of iron porphyrins, chlorins, and isobacteriochlorins has been examined by several workers,^{14,15} including ourselves.¹⁶ An equally important question for the functioning of nitrite reductases is the redox chemistry and properties of iron-nitrosyl and iron-nitrite complexes. There are several reports on the electrochemistry of iron porphyrin nitrosyls,¹⁷ as well as

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the chlorin and isobacteriochlorin analogues.¹⁸ The electrochemistry of the iron-nitrite complexes will be the subject of this report.

Over the past decade, many complexes of ferric porphyrins with anionic axial ligands have been characterized,¹⁹⁻²¹ several of which are known to form bis adducts, such as methoxide,^{22,23} fluoride,²⁴ imidazolate,^{25,26} mercaptides,^{27,28} and cyanide.^{29,30} All of the above complexes are low spin, except for the fluoro complex. In addition, the electrochemistry of iron porphyrins with a large number of anionic axial ligands has also been reported.³¹ One ligand that has been studied in much less detail is nitrite. The electrochemical behavior of iron porphyrins in the presence of nitrite has only been reported in aqueous solutions. Murphy et al. have shown that the electrolysis of an iron porphyrin in water with nitrite present leads to the production of ammonia.³² This work has been examined in more detail by Barley et al.³³ The visible spectra of iron-porphyrin-nitrite complexes in aprotic solvents have also been reported,^{34,35} where a mono-nitrite complex was described. It is the aim of this work to characterize the complex formed between iron porphyrins and nitrite and to study the electrochemical reduction of this complex in order to understand the important redox factors in the modeling of nitrite reductases.

Experimental Section

Equipment. Cyclic voltammetric data were obtained with an ECO 553 potentiostat, an EG&G Princeton Applied Research (PARC) 175 waveform generator, and a Hewlett-Packard 7045 X-Y recorder. Positive feedback was used for *iR* compensation, when required. A three-electrode IBM cell was used for all experiments, which consisted of platinum working and auxiliary electrodes and an aqueous Ag/AgCl (saturated KCl) or a Ag/0.1 M AgNO₃ (in acetonitrile) reference electrode (SRE), as noted in the work. The UV/visible spectra were obtained on a Perkin-Elmer 320 UV/visible spectrophotometer with a Perkin-Elmer 3600 data station. The NMR spectra were taken on a 60-MHz (proton) JEOL JNM-FX60Q Fourier transform NMR spectrometer. The infrared spectra were obtained on an Analect FX-6200 Fourier transform infrared spectrometer.

Chemicals. Tetraphenylchlorin (TPC) was obtained from the diimide reduction of TPP.³⁶ Tetraphenylporphyrin (TPP), octaethylporphyrin (OEP), and tetraphenylphosphonium chloride were obtained from Aldrich Chemical Co. Iron was inserted in these complexes by the FeCl₂/DMF method.^{16,37} The solvents were obtained from Aldrich Chemical

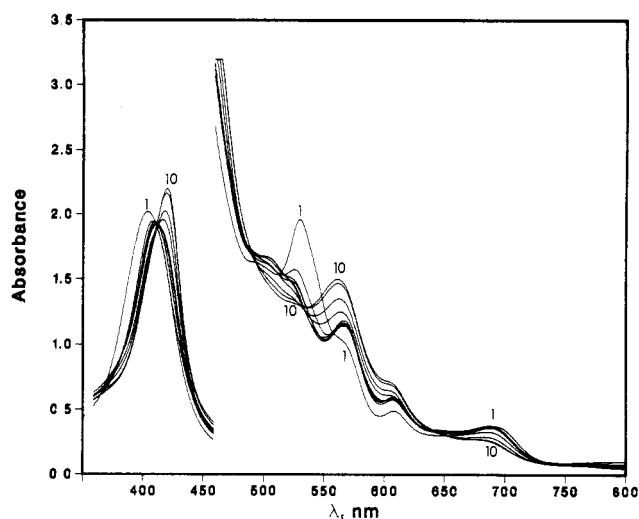


Figure 1. Visible spectra of 0.1 mM Fe(TPP)(NO₃) in DMF with various concentrations of nitrite. Concentrations of nitrite from spectra 1 to 10: 0, 0.2, 0.4, 0.5, 1, 2, 5, 10, 20, 30 mM.

Co. in the highest available purity. Tetrabutylammonium perchlorate (TBAP) was obtained from G. F. Smith Chemical Co. Tetraphenylphosphonium nitrite was obtained from the metathesis reaction of tetraphenylphosphonium chloride with sodium nitrite in water and vacuum-dried.

Procedures. All voltammetric solutions were degassed with prepurified dinitrogen that had been saturated with the solvent prior to obtaining the voltammograms. The visible spectra were obtained with two cells: a 1-cm cell for the region from 800 to 460 nm and a 0.1-cm cell for the Soret region. The determination of the formation constant from the visible spectra was accomplished by the use of the program SPECDEC,³⁸ using the IMSL library for matrix operations, as described in ref 16. The program calculated the best ϵ values for a given set of formation constant(s) and, then, adjusted the value(s) of the formation constant(s) to achieve the best fit between the observed and calculated absorbances, over the entire range of ligand concentrations. At least 10 wavelengths were used for each set of data. The concentrations of all the species at equilibrium are calculated exactly by using an iterative process with a total relative error in concentration of less than 1 ppm.

Results

Spectroscopy of Iron-Nitrite Complexes. Significant spectral changes occurred when nitrite (as Ph₄P⁺ salt) was added to Fe(TPP)(NO₃) in DMF, as shown in Figure 1. Several isosbestic points were observed over a limited range of nitrite concentrations, but none were seen over the entire concentration range, indicating that more than two chemical species were present at equilibrium. The most significant changes that were observed in the spectra were the disappearance of the 534-nm band, the appearance of a new band at 560 nm, and the shift in the Soret band from 407 to 420 nm. Similar spectral changes were observed in Me₂SO and methylene chloride. In methylene chloride, it was extremely important that the solvent, complex, and salts be anhydrous, or else the iron porphyrin will decompose to the μ -oxo complex, especially if weak axial ligands such as nitrate are used. When Fe(TPP)Cl (with excess chloride added as the tetraphenylphosphonium salt) was used instead of the nitrate complex in methylene chloride, though, the results were somewhat different: isosbestic points were observed, indicating that only two chemical species were present in significant amounts. The spectrum of Fe(TPP)Cl in methylene chloride with a high concentration of nitrite was identical with the spectrum obtained for Fe(TPP)(NO₃) for the same conditions. The reason for these differences will be discussed later in this article. It should be added that these changes were reversible, with the regeneration of the Fe(TPP)Cl spectrum when additional chloride was added to a solution that had a significant amount of the bis-nitrite complex.

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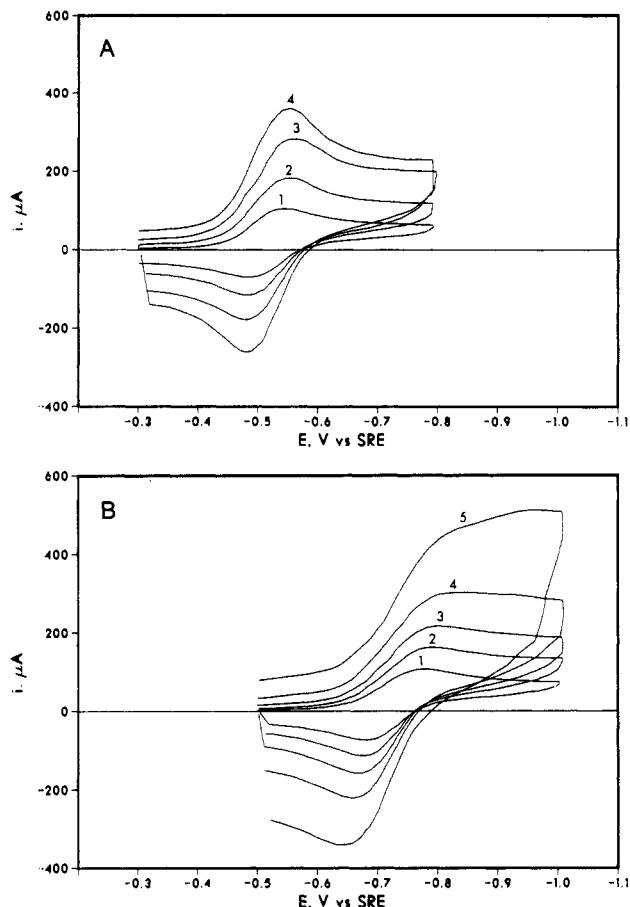


Figure 2. Cyclic voltammetry of 0.5 mM Fe(TPP)(NO₃) in DMF (platinum electrode): (A) 0 mM nitrite; (B) 20 mM nitrite. Scan rates: (1) 20, (2) 50, (3) 100, (4) 200, (5) 500 mV/s.

In order to identify the chemical nature of the species present, proton NMR studies of Fe(TPP)(NO₃) in the presence of nitrite in DMF were performed. Repeating the titration of Fe(TPP)(NO₃) with nitrite in DMF-*d*₇, one observed that the 66.6-ppm pyrrole resonance for Fe(TPP)(NO₃) disappeared and a new resonance appeared at -16.2 ppm. Further additions of nitrite led to the appearance of a new resonance at -16.0 ppm and a decrease in the -16.2-ppm resonance. The NMR results in DMF were unaffected by the presence of water (200 mM), while there were slight changes in the visible spectrum with the Soret band shifting to 423 nm and the 560-nm band shifting to 570 nm. The NMR spectrum of Fe(TPP)(NO₃) in the presence of nitrite was difficult to obtain in CD₂Cl₂ due to the formation of the μ -oxo complex at the concentrations used, probably due to the presence of water. But, at -44 °C, an NMR spectrum similar to what was seen in DMF-*d*₇ was obtained with a resonance for the pyrrole protons at -30 ppm with 1 equiv of nitrite added. Further addition of nitrite led to a new resonance at a somewhat smaller chemical shift, which was poorly resolved from the original -30-ppm resonance due to the broadness of the peaks.

The infrared spectra of Fe(TPP)(NO₃) in the presence of nitrite was obtained with CH₂Cl₂ or CD₂Cl₂ as solvent. The first addition of nitrite led to the appearance of absorption bands at 1345 and 1358 cm⁻¹. At high concentrations of nitrite, the lower energy band became more intense, at the expense of the 1358-cm⁻¹ band. No new bands were observed from 1000 to 1100 cm⁻¹, where there was a clear window in the solvent, nor were there any bands at 860 or 890 cm⁻¹, which are indicative of the μ -oxo iron complex.

Electrochemistry of Iron Porphyrins and Chlorins in the Presence of Nitrite. The spectral changes that were observed for ferric porphyrins in the presence of nitrite should be reflected in their voltammetric behavior if nitrite complexes were formed. This was indeed the case. The electrochemical reduction of Fe^{III}(TPP)(NO₃) in the absence and presence of nitrite with DMF or

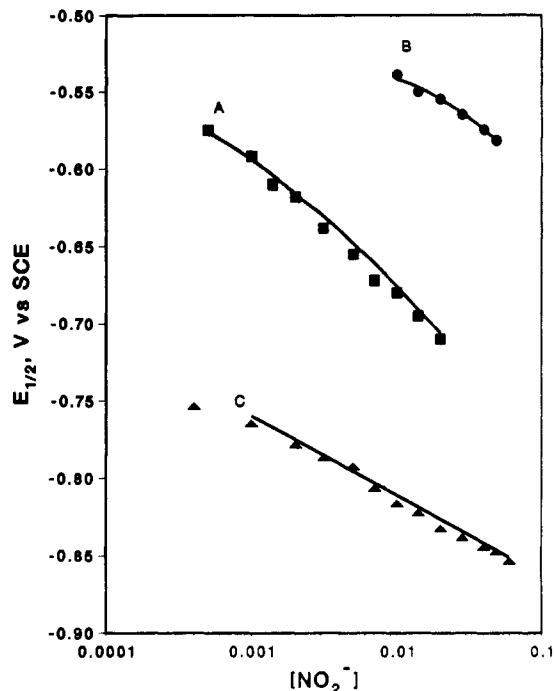


Figure 3. Variation of $E_{1/2}$ of ferric/ferrous reduction as a function of the concentration of nitrite: (A) Fe(TPP)(NO₃) in DMF; (B) Fe(TPP)(NO₃) in Me₂SO; (C) Fe(OEP)(NO₃) in DMF. For plots A and B the points are the observed $E_{1/2}$ while the theoretical line from the data in Table I and eq 3. In plot C the points are the observed $E_{1/2}$ while the line is the least-squares-fit line with a slope of 52 mV.

Me₂SO as the solvent was reversible at slow scan rates, as is shown in Figure 2, with some effect of slow electron transfer or ligand association/dissociation kinetics. The $E_{1/2}$ values depended upon the concentration of nitrite, shifting to more negative potentials as the nitrite concentration was increased, as is shown in Figure 3. The slope, especially at higher nitrite concentrations, was greater than 59 mV/log [NO₂⁻], indicating that more than one nitrite ion was lost upon reduction of the ferric complex.

When the scan rate was increased, the ferric/ferrous reduction wave split into two waves (see Figure 2B), indicating that two different species were present at equilibrium, which slowly interconverted. Since neither wave had a potential that was the same as the original nitrate complex, there must be two nitrite species present. This was consistent with the visible spectroscopy data, which showed no isosbestic points. The presence of a single anodic wave indicated that only one ferrous species was present. Similar results were seen in Me₂SO, but higher concentrations of nitrite were needed to see the effect shown in Figure 2B. The same results were seen for Fe(TPC)Cl in both solvents. In methylene chloride, the ferric/ferrous wave was irreversible, with no anodic peak seen for Fe(TPP) and Fe(TPC) complexes.

The voltammetry of Fe(OEP)(NO₃) in DMF was similar to but not identical with that of Fe(TPP)(NO₃). At low concentrations of nitrite (0.4 mM), two waves were observed for the ferric/ferrous reduction even at low scan rates. Between 0.4 and 5 mM nitrite, the wave became much more reversible in shape, especially at low scan rates. By 5 mM nitrite, the peak for the first wave almost disappeared, and a single cathodic wave was seen. But, unlike that for Fe(TPP)(NO₃), the slope of the $E_{1/2}$ -log [NO₂⁻] plot was 52 mV, which was much smaller than the Fe(TPP)(NO₃) results (see Figure 3).

In addition to the ferric/ferrous and Fe(II)/Fe(I) waves, a new wave was observed at about -0.9 V vs. SCE (see Figure 4). This appears at the potential that is expected for Fe(TPP)(NO) or nitric oxide.¹⁷ It was difficult to unambiguously determine which species gave rise to that wave, but most of the evidence indicates that NO was formed initially. While controlled-potential coulometry of Fe(TPP)(NO₃) in methylene chloride and DMF in the presence of nitrite leads ultimately to Fe(TPP)(NO), which was detected both spectrally and voltammetrically, there are several pieces of

Table I. Formation Constants for Anionic Ferric-Porphyrin Bis Complexes

reactant complex	product complex	solvent	K_1^a	K_2^a	ref
Fe(TPC)Cl	Fe(TPC)(NO ₂) ₂ ⁻	CH ₂ Cl ₂	0.07 (0.02)	110 (10)	tw ^b
Fe(TPP)Cl	Fe(TPP)(NO ₂) ₂ ⁻	DMF	8500 (800)	270 (10)	tw
Fe(TPC)Cl	Fe(TPC)(NO ₂) ₂ ⁻	DMF	7500 (2000)	133 (8)	tw
Fe(TPP)(NO ₃)	Fe(TPP)(NO ₂) ₂ ⁻	CH ₂ Cl ₂ ^c	0.17 (0.08)	61 (1)	tw
Fe(TPP)(NO ₃)	Fe(TPP)(NO ₂) ₂ ⁻	DMF	2.0 × 10 ^{4d}	127 (7)	tw
				200 ^d	
Fe(TPP)(NO ₃)	Fe(TPP)(NO ₂) ₂ ⁻	Me ₂ SO	50	30 (1)	tw
Fe(OEP)(NO ₃)	Fe(OEP)(NO ₂) ₂ ⁻	DMF	large	2200 (200)	tw
Fe(TPP)F	Fe(TPP)(F) ₂ ⁻	CH ₂ Cl ₂		4000	39
Fe(PP)Cl ^e	Fe(PP)(CN) ₂ ⁻	Me ₂ SO	1.9 × 10 ⁴	1100	29

^aUncertainties given in parentheses. ^btw = this work; temperature 25 °C unless noted. ^ctemperature 0 °C. ^dDetermined voltammetrically by eq 3. ^ePP = protoporphyrin.

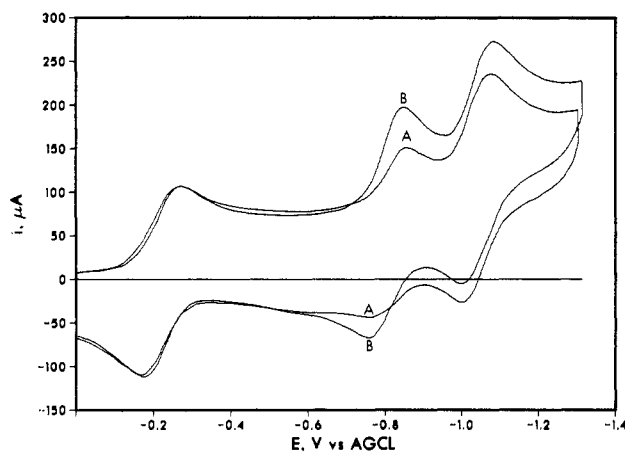
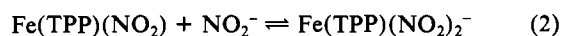


Figure 4. Cyclic voltammetry of Fe(TPP)Cl in DMF (scan rate 50 mV/s; platinum electrode; 0.1 M TBAP): (A) 0.1 mM Fe(TPP)Cl with 5 mM nitrite; (B) 0.1 mM Fe(TPP)Cl + 0.1 mM Fe(TPP)(NO) with 5 mM nitrite.

evidence that lead us to conclude that this wave in DMF is due to NO. First, the formation of this new wave, which is rather large, does not cause the ferric/ferrous wave to become irreversible, nor does it cause the loss of the Fe(II)/Fe(I) wave. If Fe(TPP)(NO) were to be formed, there would be little or no free ferrous porphyrin to be reoxidized on the reverse scan of the first wave. Similar reasoning would lead us to expect the ferrous reduction wave to disappear. Second, the addition of authentic Fe(TPP)(NO) to a solution containing Fe(TPP)(NO₃) and nitrite leads to a small but significant shift in the potential of this new wave (see Figure 4). In addition, Fe(TPP)(NO) is much more reversible than the new wave. Third, a small amount of nitric oxide would probably give rise to a significant amount of current due to the much higher diffusion coefficient of NO when compared to those of iron porphyrins. The mechanism for the formation of nitric oxide and the nitrosyl has not yet been completely elucidated.

Discussion

The absorbance changes in Figure 1 were fit to two equilibrium cases by using SPECDEC: (I) the formation of a mono-nitrite complex only, and (II) the formation of both a mono-nitrite and a bis-nitrite complex. After the best fit was obtained, the residual errors for case I were systematic (i.e., the deviations at low concentrations were always opposite in sign to the deviations at high concentration) and larger than for case II. By contrast, the residual errors the case II were random. Therefore, the quantitative analysis of the spectra confirmed the qualitative observation that indicated that more than one nitrite complex was present, as shown in reactions 1 and 2. The first formation constant

$$\text{Fe(TPP)(DMF)}_2^+ + \text{NO}_2^- \rightleftharpoons \text{Fe(TPP)(NO}_2) + 2\text{DMF} \quad (1)$$


(reaction 1), K_1 , was too large to be measured spectroscopically, while the second one (reaction 2), K_2 , was found to be 127. One

Table II. Visible Spectra of Ferric-Porphyrin Bis Complexes

complex	solvent	Soret, nm	other visible bands, nm	ref
Fe(TPP)(NO ₂) ₂ ⁻	DMF	420	560, 608 (sh), 690 (sh)	tw ^a
	Me ₂ SO	420	528, 687	tw
	CH ₂ Cl ₂	426	540, 576 (sh), 602 (sh)	tw
Fe(TPC)(NO ₂) ₂ ⁻	DMF	420	560, 634	tw
	Me ₂ SO	418	536 (sh), 562, 636	tw
	EtCl ₂	420	552, 601, 620	tw
Fe(OEP)(NO ₂) ₂ ⁻	DMF	380	502 (sh), 534, 590 (sh), 630 (sh)	tw
	CH ₂ Cl ₂	375	414, 530, 560, 634	tw
Fe(TPP)(4MeIm) ₂ ⁻	DMA ^b	425	558, 598	26
Fe(TPP)(CN) ₂ ⁻	MeOH	424	539, 560, 596	30
Fe(TPP)(OMe) ₂ ⁻	Me ₂ SO	438	550, 597, 638	23
Fe(TPP)(F) ₂ ⁻	Me ₂ SO		531, 590, 631	31
Fe(TPP)(4MeImH) ₂ ⁺	DMA ^b	416	458 (sh), 554, 578 (sh)	26

^atw = this work. ^bDMA = dimethylacetamide.

should note that in DMF weak ligands such as nitrate are displaced by the solvent, and even for chloride, the equilibrium only slightly favors the chloro complex.³¹ Similar results were observed in methylene chloride and Me₂SO, as well as for Fe(TPC)Cl and Fe(OEP)(NO₃). The calculated formation constants are summarized in Table I. The visible absorption maxima for the bis-nitrite complexes studied are summarized in Table II.

When chloride was present in excess in noncoordinating solvents, significant amounts of Fe(TPP)(NO₂) were not present at equilibrium. Once the nitrite concentration was sufficient to displace chloride, the nitrite concentration was high enough to form the bis complex. As a result, only Fe(TPP)Cl and Fe(TPP)(NO₂)₂⁻ were present, except for very low concentrations of chloride ion, giving rise to the observed isosbestic points. In fact, if one assumes that both the mono and bis complexes were formed, the program will reduce the value of K_1 until it is too small to be significant. Similar results were observed for Fe(TPC)Cl and Fe(OEP)Cl, which are summarized in Tables I and II.

In addition to the absorbance changes that were observed with the addition of nitrite, the shifts in the Soret band were consistent with the formation of a bis-anionic complex. The red shift in the Soret band has been correlated with the formation of an anionic metal porphyrin complex.⁴⁰ The results for Fe(L)(NO₂)₂⁻ where L = TPP, TPC, and OEP are shown in Table II, along with literature values for related bis complexes. When L = TPC, the results were similar to those for L = TPP.

The NMR results were also consistent with the formation of two nitrite complexes. In particular, the pyrrole resonance of a low-spin Fe^{III}TPP complex is invariably upfield from Me₄Si, as is seen in the Fe^{III}TPP bis-imidazole complex with a resonance of -16.6 ppm at room temperature.⁴¹ No new resonances appeared in the region indicative of a high-spin ferric complex (60–80

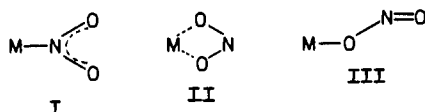
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ppm), nor was any resonance seen for the μ -oxo complex. Therefore, these results show that both the mono- and bis-nitrite complexes are *low-spin*. There are two other examples in the literature for low-spin five-coordinate ferric-porphyrin complexes: the mono-cyano complex of ferric protoporphyrin,²⁹ and ferric tetrakis(4-methoxyphenyl)porphyrin hydrosulfide.⁴² By contrast, other complexes that form bis-coordinated ferric porphyrin complexes are high spin in the mono complex, such as Fe(TPP)F³⁹ and Fe(TPP)(OMe).²³ Of the bis-anionic complexes that have been studied, only the bis-fluoro-complex remains in the high-spin ferric state with a pyrrole proton signal at 85 ppm, compared to 80 ppm for the mono-fluoro complex.³⁹

While the overall stoichiometry and spin states of the nitrite complexes can be determined by NMR and visible spectroscopy, the structures of the mono and bis complexes can be inferred from infrared studies. There are three possibilities for the structure of the monomeric nitrite complexes:



where I, II, and III are the nitro, chelated nitro, and nitrito complexes, respectively. Species I and II can be distinguished from III on the basis of the two stretching frequencies, ν_s and ν_a . For nitro complexes, the two frequencies are similar, typical values being 1320–1340 cm^{-1} for ν_s and 1370–1470 cm^{-1} for ν_a . This is due to the equivalence of the N—O bond orders in the nitro case. For nitrito bonding, the two N—O bonds have very different strengths and the N—O stretching frequencies are typically in the ranges 1400–1485 cm^{-1} for N=O and 1050–1110 cm^{-1} for N—O.⁴³ No bands were seen that were indicative of the nitrito complex, while the IR spectra observed were more consistent with I and II. The low-spin nature of the mono-nitrite complex makes us favor I over II, because II should yield an NMR spectrum much more similar to that of the nitrate complex, which is high spin.

The shift in the ferric/ferrous half-wave potential, $E_{1/2}$, was also consistent with the formation of mono- and bis-nitro ferric complexes and a ferrous complex uncoordinated with nitrite. The relationship between $E_{1/2}$ and the concentration of nitrite is

$$(E_{1/2})_c = (E_{1/2})_u - 0.059 \log (1 + K_1[\text{NO}_2^-] + K_1K_2[\text{NO}_2^-]^2) \quad (3)$$

where $(E_{1/2})_c$ and $(E_{1/2})_u$ refer to the $E_{1/2}$ of the iron porphyrin complexed and uncomplexed with nitrite, respectively. In Figure 3, the theoretical lines for Fe(TPP)(NO₃) in DMF and Me₂SO are shown, along with the experimental points. From these data, values of K_1 and K_2 of 2.0×10^4 and 200, respectively, were found for Fe(TPP)(NO₃) in DMF. The K_2 value compares well with the spectroscopically determined value. Similar results were observed in DMF and Me₂SO for Fe(TPP)Cl and Fe(TPC)Cl. Two waves were seen at fast scan rates because the interconversion of the mono and bis-nitro complexes was too slow to form the mono-nitrite complex, which is easier to reduce. For Fe(OEP)(NO₃) in DMF, a least-squares-fit line was drawn through the data in Figure 3, and a slope of 52 mV was obtained. This was close to 59 mV, which was the value expected for a change of 1 in ligand number (theoretical value 59 mV). Because spectroscopic analysis shows that the bis-nitro ferric complex was formed quite readily at these concentration levels, Fe^{II}(OEP)(NO₂)⁻ must be present.

A comparison of K_1 values is relatively difficult because of the large dependence on the axial ligand. As expected, the value of

Table III. Half-Wave Potentials of Anionic Iron-Porphyrin Bis Complexes

complex	solvent	$E_{1/2}^a$	ref
Fe(TPP)(NO ₂) ₂ ⁻	DMF	-0.45 ^{b,c}	tw ^d
Fe(OEP)(NO ₂) ₂ ⁻	DMF	-0.83 ^b	tw
Fe(TPP)(F) ₂ ⁻	Me ₂ SO	-1.10	31
Fe(TPP)(4MeIm) ₂ ⁻	DMA ^e	-0.75 ^c	26

^a $E_{1/2}$ of Fe^{III}/Fe^{II} redox couple, V vs. SCE; temperature 25 °C. ^b With 20 mM nitrite present. ^c $E_{p,c}$ values. ^d tw = this work. ^e DMA = dimethylacetamide.

K_1 is significantly smaller in Me₂SO than in DMF because nitrite must displace the coordinated solvent molecule in Me₂SO. There is essentially no effect of solvent on K_2 as shown in Table I for Fe(TPP)(NO₃) for Me₂SO, DMF, and methylene chloride, where the K_2 values are 30, 270, and 61, respectively. A comparison of the K_2 values for nitrite and other anionic ligands, as summarized in Table I, shows that nitrite is significantly weaker than the other anions. For example, the K_2 values for the bis-fluoro are 20–40 times larger than those for the bis-nitro, while the bis-cyano is about 5–10 times stronger. There were little measurable differences between TPP and TPC, while the Fe(OEP)(NO₂)₂⁻ complex was much stronger than the TPP analogue. This is in keeping with the results for the pyridine complexes¹⁶ and CO binding.⁴⁴

The electrochemical reduction of the bis-nitro complex occurs at a much lower potential than other anionic bis-coordinated iron porphyrin complexes. As is summarized in Table III, the bis-fluoro complex reduces irreversibly at -1.10 V, while the bis-imidazolate complex reduces reversibly at -0.75 V. The irreversibility of the bis-fluoro complex was attributed to the rapid loss of fluoride to form the mono-fluoro ferrous complex, as was observed for the bis-nitro complexes of TPP and TPC in this work. The lower potential for the bis-imidazolate complex, which was reduced in the presence of excess imidazolate, was rationalized on the basis of a stronger π -interaction between the iron and the ligand. Similar π -bonding is available in nitrite and may be responsible for the lower potential.

Work is in progress in our laboratory to examine the kinetics of the ligand exchange (mono to bis) reactions, as well as the details of the formation of nitric oxide or nitrosyl. The difficulty in the formation of the nitrosyl may be due to the fact that the most detailed work done so far in our laboratory is in coordinating solvents such as DMF and Me₂SO, which must be displaced to form the nitrosyl. There is evidence in our laboratory that Fe(TPP)(NO) is formed in methylene chloride on the voltammetric as well as the coulometric time scale. What is not clear at this time is the steps in the reduction of nitrite. There are several possibilities: (a) nitrite may bridge ferric and ferrous complexes, with the ferrous being oxidized while the nitrite is reduced to NO; (b) the mono-nitrite ferrous species may be present in small amounts, which is oxidized slowly to ferric, with the nitrite being reduced. Trace amounts of proton donors may stimulate this reaction. If a ferric species is involved, it is not clear at this time if the mono- or bis-nitro complex is most reactive. Detailed examination of the electrochemistry of these complexes in the presence of nitrite should clarify this problem.

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Registry No. Fe(TPC)(NO₂)₂⁻, 102494-80-4; Fe(TPP)(NO₂)₂⁻, 102494-81-5; Fe(OEP), 61085-06-1.

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