of *S. aureus* (Table II). The relative affinities do not correlate with the complex stability, as can be seen from the data in Table II.

Conclusion

We have shown, for the first time, that directed fermentation of siderophore-producing microorganisms is a powerful biosynthetic approach to "unnatural", structurally modified siderophores. By feeding suitable diamino acid and diamine precursors to cultures of *S. olivaceus* Tü 2718, 13 new desferrioxamine siderophores have been isolated by a three-step chromatographic procedure. The new siderophores are analogues of the "natural", macrocyclic trihydroxamic acid desferrioxamine E, from which they differ in ring size and by substitution of CH_2 groups of the diaminopentane moieties by oxygen or sulfur atoms or by amide bonds. Two of the new desferrioxamines are dihydroxamic acids lacking one of the *N*-hydroxyl groups.

Spectrophotometric titrations and EDTA competition experiments performed with the trihydroxamic acid desferrioxamines have shown that the stability of the complexes decreases steadily as the structure of the ligand deviates from that of desferrioxamine E. By far the lowest complex stability is found for the structurally most deviant dihydroxamic acid, desferrioxamine X_5. It is demonstrated that desferrioxamine X_5 forms two types of ferric complexes, a monomer FeL^+ at low pH and a dimer Fe_2L_3 at high pH. All of these desferrioxamines are effective iron transport agents. There is no correlation between the complex stability and biological activity.

Acknowledgment. This investigation was supported by grants from the Deutsche Forschungsgemeinschaft (SFB 323) and U.S. National Institutes of Health (AI11744). Doctorate stipends from the Studienstiftung des Deutschen Volkes (S.K.-R.) and the DE-CHEMA (J.M.) are gratefully acknowledged.

Highly Oxidized Iron Complexes of *N*-Methyltetra-*p*-tolylporphyrin

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Abstract: Two different, highly oxidized iron complexes of *N*-methyltetra-*p*-tolylporphyrin (*N*-MeTTPH) have been detected by ^1H and ^2H NMR spectroscopy after oxidation with *m*-chloroperoxybenzoic acid. In CH_2Cl_2/CH_3OH (4:1, v/v) in the presence of sodium methoxide (*N*-MeTTP)$Fe^{II}Cl$ is converted to (*N*-MeTTP)$Fe^{II}(OCH_3)$ and then to (CH_3O)(*N*-MeTTP)$Fe^{IV}{=}O$ upon addition of the peroxyacid. The latter is observable over the temperature range −90 to 0 °C, has a magnetic susceptibility of 2.9 μ_B ($S = 1$), and is reduced by phenyldimethylphosphine to (*N*-MeTTP)$Fe^{II}(OCH_3)$. In the absence of sodium methoxide, (*N*-MeTTP)$Fe^{II}Cl$ is oxidized by the peroxyacid to form a very unstable species observable from −90 to −75 °C whose ^1H NMR spectrum shows large hyperfine shifts for the meso aryl substituents that are consistent with the presence of a π-*N*-methylporphyrin radical in the product.

Introduction

N-Alkylated[1] porphyrins are formed during the inactivation of cytochrome P-450 by a variety of chemical agents.[2] Inactivation during the epoxidation of terminal olefins produces adducts in which the terminal carbon of the olefin is bound to a pyrrole nitrogen and a hydroxyl group is bound to the internal carbon.[3]

Considerable study of the cytochrome P-450 cycle in the enzyme itself and in model systems have led to the hypothesis that the active oxidant is a highly oxidized iron porphyrin generally described as a ferryl $(Fe^{IV}{=}O)^{2+}$ ion coordinated to an oxidized porphyrin in its π-radical form (ie., $P^{\bullet}Fe^{IV}{=}O$).[4,5] This intermediate, which cannot be directly observed during the operation of cytochrome P-450, is felt to be at the same level of oxidation as the observable intermediate compound I that is present during turnover of horseradish peroxidase.[6]

Synthetic meso-tetraarylporphyrins that are capable of catalyzing the epoxidation of olefins with nonphysiological oxidants, iodosoarenes, or hypochlorite also can undergo N-alkylation during the catalytic cycle.[7-12] It has been noted, however, that in these cases N-alkylation does not completely inhibit epoxidation activity.[10,11] That is, the N-alkylated porphyrin iron complex retained some lesser activity as a epoxidation catalyst. This suggests that highly oxidized iron complexes of these N-substituted porphyrins may exist. Here we describe efforts to directly detect such species. Our efforts have concentrated on examining the reactivity of the high-spin, five-coordinate Fe^{II} complex **1** toward another non-

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[†] University of California, Davis.

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(1) Lavallee, D. K. *The Chemistry and Biochemistry of N-substituted Porphyrins*; VCH Publishers: New York, 1987.

(2) Ortiz de Montellano, P. R.; Reich, N. O. In *Cytochrome P-450. Structure, Mechanism, and Biochemistry*; Oritz de Montellano, P. R., Ed.; Plenum Press: New York, 1986; p 273.

(3) Ortiz de Montellano, P. R.; Mico, B. A. *Mol. Pharmacol.* **1980**, *18*, 128.

(4) McMurry, T. J.; Groves, J. T. In *Cytochrome P-450. Structure, Mechanism and Biochemistry*; Ortiz de Montellano, P. R., Ed.; Plenum Press: New York, 1986; p 1.

(5) Dawson, J. H. *Science* **1988**, *240*, 433.

(6) Dunford, H. B. In *Peroxidases in Chemistry and Biology*; Everse, J., Everse, K. E., Grisham, M. B., Eds.; CRC Press: Boca Raton, FL, 1991; Vol. II, p 1.

(7) Mashiko, T.; Dolphin, D.; Nakano, T.; Traylor, T. G. *J. Am. Chem. Soc.* **1985**, *107*, 3735.

(8) Mansuy, D.; Devocelle, L.; Artland, J.; Battioni, J. *Nouv. J. Chim.* **1985**, *9*, 711.

(9) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 7861.

(10) Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *J. Am. Chem. Soc.* **1987**, *109*, 3625.

(11) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2977.

(12) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *J. Am. Chem. Soc.* **1990**, *112*, 2986.

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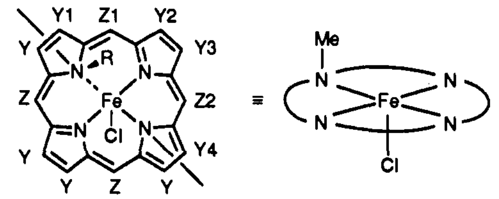
Table I. ^{1}H and ^{2}H NMR Data for Iron Complexes

compound	chemical shift, δ (ppm) pyrr	*N*-Me	*p*-Ar	*m*-Ar	*o*-Ar	*T* (°C)	ref
1, (*N*-MeTTP)Fe^{II}Cl	62.8, 42.5, −6.3 (2)	193			18.5	−90	18
2, (*N*-MeTTP)Fe^{II}(OCD$_3$)	47.7, 43.6, −7.6, −20.8	*a*			13.1	−90	this work
2, (*N*-{Me-*d*$_3$}TTPpyrrole-*d*$_8$)Fe^{II}(OCH$_3$)	48, 44, −8, −21	252				−90	this work
(*N*-MeTTP)Fe^{II}(OC$_6$H$_4$CH$_3$-*p*)	43.2, 41.2, −6.1, −16.7	197			12.9	−60	this work
5, [(*N*-MeTTP)Fe^{III}Cl]$^+$	128, 92, 79, 2	272				−50	21
[(*N*-MeTTP)Fe^{III}(CN)$_2$]$^-$	0.0, −31.5, −34.2, −56.9	−61				−90	21
3, (CD$_3$O)(*N*-MeTTP)Fe^{IV}=O	−1.6, −6.3, −7.6, −17.1	*b*		9.8, 10.5 (2),^{c} 11.0		−90	this work
3, (CH$_3$O)(*N*-{Me-*d*$_3$}TTP-pyrrole-*d*$_8$)Fe^{IV}=O	−1.6, −6.3, −7.6, −17.1	−59					this work
4, (*m*-ClC$_6$H$_4$CO$_2$)(*N*-MeTTP)Fe^{IV}=O	−8.8, −16			8.8, 10.5, 11.0, 12.2		−90	this work
4, (*m*-ClC$_6$H$_4$CO$_2$)(*N*-MeTTP-pyrrole-*d*$_8$)Fe^{IV}=O	2.5, 0.3, −6.9, −10.8					−60	this work
4, (*m*-ClC$_6$H$_4$CO$_2$)(*N*-{Me-*d*$_3$}TTP)Fe^{IV}=O		−49.5				−60	this work
6, from (*N*-MeTTP)Fe^{II}Cl	−152		{125.8 100.8}^{d}	58.8, 58.2 49.7, 47.7	−72.5 −74.3 (2)^c −76.2	−90	this work
6, from (*N*-MeT{T-*d*$_7$}P)Fe^{II}Cl			{127.2, 102.3}	61.1, 51.4	−70.9	−90	this work
6′, from (*N*-MeT{3,5-Me$_2$C$_6$H$_3$}P)Fe^{II}Cl	−154		−71.2, −85.1	−12.4, −13.3, −15.8, −17.8	−63.9, −64.8, −67.4, −69.9	−90	this work
(TMP)Fe^{IV}=O	8.4		[2.6]^d	6.4, 6.6	{3.3}^{d}		28
(*N*-MeIm)(TPP)Fe^{IV}=O	5.05		7.9	7.9	9.2	−80	29
(Me$_3$N)(TPP)Fe^{IV}=O	1.1					−76	32
(CD$_3$O)(TMP)Fe^{IV}=O	0.1, −4.1		{2.7}^{d}		{1.5 3.0}^{d}	−30 −90	this work
[(TMP$^\bullet$)Fe^{IV}=O]$^+$	−27		{11.1}^{d}	68	{26.24}^{d}	−77	14
[(TTP$^\bullet$)Fe^{III}Cl](SbCl$_6$)	64.8		{−30.5}^{d}	−14.7	48	25	37
(TTP$^\bullet$)Fe^{III}(OClO$_3$)$_2$	31.6		{0.1}^{d}	31.6	−16.9	25	37
[(TMP)Fe^{IV}(OCH$_3$)$_2$]	−37.5		{2.86}^{d}	7.72	{2.4}^{d}	−78	34
(TTP)Fe^{IV}(Ph)Br	−60		{4.3}^{d}	9.5	9.8, 10.3	−50	35

^{a}Not observed. ^{b}Not observed at −90 °C, −41 ppm at −30 °C. ^{c}Intensity twice that of related protons. ^{d}Methyl resonances.

physiological oxidant, *m*-chloroperoxybenzoic acid. This oxidant has been shown to oxidize TMPFe^{III}Cl to [(TMP$^\bullet$)Fe=O]$^+$, a green species at the oxidation level of HRP compound I.[13-15]



1: Z = *p*-tolyl, Y = H, R = CH$_3$

There exist significant parallels in the complexes that iron forms with tetraarylporphyrins and with *N*-methyltetraarylporphyrins. For iron(II), five-coordinate, high-spin ($S = 2$) complexes are known for both ligands ([(TPP)Fe^{II}(OR)]$^-$ [16] and (*N*-MeTPP)-Fe^{II}Cl)[17,18]. With iron(III) there are related five-coordinate, high-spin ($S = {}^5/_2$) complexes ((TPP)Fe^{III}Cl[19,20] and [(*N*-MeTPP)Fe^{III}Cl]$^+$ [21,22] and low-spin ($S = {}^1/_2$), six coordinate complexes ([(TPP)Fe^{III}(CN)]$^{2-}$ [23,24] and (*N*-MeTTP)Fe^{III}(CN)$_2$]^{21}). Additionally, both ligands form antiferromagnetically coupled Fe^{III} complexes with an oxo bridge.[25,26] Here, we extend these parallels to show that the *N*-methyltetraarylporphyrin ligand, like the corresponding porphyrin ligand, is capable of forming more highly oxidized species.

Results

Axial Ligands Exchange and the Formation of (*N*-MeTTP)-Fe^{II}(OCD$_3$) (2). Treatment of (*N*-MeTTP)Fe^{II}Cl (**1**) with sodium methoxide-*d*$_3$ in a solvent mixture of dichloromethane-*d*$_2$/methanol-*d*$_4$ (4:1, v/v) at −90 °C results in the formation of (*N*-MeTTP)Fe^{II}(OCD$_3$) (**2**) as shown in Figure 1. Trace A shows the ^{1}H NMR spectrum of (*N*-MeTTP)Fe^{II}Cl. This spectrum has been previously analyzed, and the component resonances have been assigned.[18] In the dichloromethane/methanol solvent, the two upfield pyrrole resonances are unresolved. Trace B shows the effect of adding 5 equiv of sodium methoxide. The resonance pattern for an iron(II) complex of an N-substituted porphyrin is retained but shifted in an upfield direction. Four pyrrole resonances are clearly resolved, two upfield at −22 and −8 ppm and two downfield at 44 and 48 ppm. These have been unambiguously identified by observing them in the ^{2}H NMR spectrum of the pyrrole-*d*$_8$-substituted analogue. The resonance of the *N*-methyl

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(13) Groves, J. T.; Haushalter, R. C.; Nakamura, M.; Nemo, T. E.; Evans, B. J. *J. Am. Chem. Soc.* **1981**, *103*, 2884.
(14) Balch, A. L.; Latos-Grażyński, L.; Renner, M. W. *J. Am. Chem. Soc.* **1985**, *107*, 2983.
(15) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8443.
(16) Nasri, H.; Fischer, J.; Weiss, R.; Bill, E.; Trautwein, A. *J. Am. Chem. Soc.* **1987**, *109*, 2549.
(17) Anderson, O. A.; Kopelove, A. B.; Lavallee, D. K. *Inorg. Chem.* **1980**, *19*, 2101.
(18) Balch, A. L.; Chan, Y.-W.: La Mar, G. N.; Latos-Grażyński, L.; Renner, M. W. *Inorg. Chem.* **1985**, *24*, 1437.
(19) Hoard, J. L.; Cohen, G. H.; Glick, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 1992.
(20) La Mar, G. N.; Walker, F. A. *J. Am. Chem. Soc.* **1973**, *95*, 6950.
(21) Balch, A. L.; Cornman, C. R.; Latos-Grażyński, L.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 7552.
(22) Balch, A. L.; La Mar, G. N.; Latos-Grażyński, L.; Renner, M. W. *Inorg. Chem.* **1985**, *24*, 2432.
(23) Collins, D. M.; Countryman, R.; Hoard, J. L. *J. Am. Chem. Soc.* **1972**, *94*, 2066.
(24) Satterlee, J. D.; La Mar, G. N. *J. Am. Chem. Soc.* **1976**, *98*, 2804.
(25) Wysłouch, A.; Latos-Grażyński, L.; Grzeszczuk, M.; Drabent, K.; Bartczak, T. *J. Chem. Soc., Chem. Commun.* **1988**, 1377.
(26) Bartczak, T.; Latos-Grażyński, L.; Wysłouch, A. *Inorg. Chim. Acta* **1990**, *171*, 205.

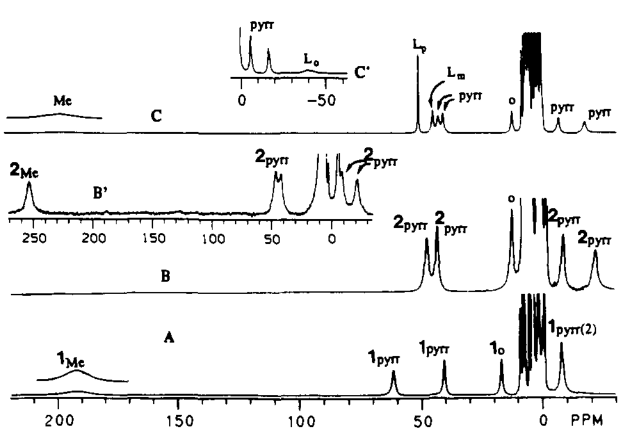

Figure 1. Trace A: ^{1}H NMR spectrum from a solution of (N-MeTTP)Fe^{II}Cl in dichloromethane-d_2/methanol-d_4 (4:1, v/v) at -90 °C. Trace B: ^{1}H NMR spectrum from the same solution after the addition of 5 equiv of sodium methoxide at -90 °C. Trace B′: ^{2}H NMR spectrum from a similar solution of (N-{Me-d_3}TTP-d_8)Fe^{II}Cl in the presence of excess sodium methoxide-d_3 at -90 °C. Trace C: ^{1}H NMR spectrum of a solution of (N-MeTTP)Fe^{II}Cl and 5 equiv of sodium p-cresolate at -60 °C in toluene-d_8/methanol-d_4 (9:1, v/v). Resonances due to (N-MeTTP)Fe^{II}Cl and (N-MeTTP)Fe^{II}(OCD$_3$) are labeled 1 and 2, respectively, with subscripts identifying resonance assignments: Me, the N-methyl protons: pyrr, the pyrrole protons; o, the ortho protons of the p-tolyl substituents.

substituent has been identified by observing the ^{2}H NMR spectrum of (N-CD$_3$TTP)Fe^{II}Cl in the presence of sodium methoxide as shown in the inset of trace B of Figure 1. NMR spectral parameters for **2** and other relevant complexes are collected in Table I.

The magnetic susceptibility of (N-MeTTP)Fe^{II}OCD$_3$ determined in dichloromethane/methanol (4:1, v/v) at -90 °C by the Evans method[27] is 5.0 (2) μ_B. This is similar to the value of 4.9 (2) μ_B measured for (N-MeTTP)Fe^{II}Cl under similar conditions. A value of 5.2 μ_B (at an unspecified temperature) has previously been reported for (N-MeTPP)Fe^{II}Cl.[17]

In the basic solution in which it is formed, (N-MeTTP)Fe^{II}(OCD$_3$) is unstable to warming. Above -90 °C, it gradually decomposes to form N-MeTTPH through the loss of iron.

No resonance due to the axial methoxide ligand of **2** has been observed. In order to detect axial ligand resonances of a compound with a related oxygen donor ligand, the addition of sodium p-cresolate to **1** was examined under related conditions. The ^{1}H NMR spectrum obtained by the addition of 5 equiv of sodium p-cresolate to **1** in toluene-d_8/methanol-d_4(9:1, v/v) at -60 °C is shown in trace C of Figure 1. Trace C′ shows an expansion of the region from 0 to -50 ppm. The spectrum is assigned to (N-MeTTP)Fe^{II}(OC$_6$H$_4$CH$_3$-p), the product of anionic ligand exchange. The pattern of porphyrin pyrrole resonances closely parallels those seen for **2** as expected since the nature of the axial donors is similar. Three additional resonances due to the axial p-cresolate ligand are also observed. On the basis of its intensity the resonance at 50 ppm is assigned to the para methyl protons. The two equally intense resonances at 45 and -45 ppm then must be due to the meta and ortho protons. The upfield resonance is assigned to the ortho protons because of its larger line width. This assignment is also consistent with the expectations of π spin delocalization. The intensity of these axial ligand resonances, when compared to the pyrrole resonances, indicates that only one axial ligand is present.

Other aspects of ligand exchange for **1** in a dichloromethane/methanol mixture have been examined. Addition of 15 equiv of sodium m-chlorobenzoate to **1** yields spectral evidence for only limited exchange; a considerable amount of unreacted **1** remains. Addition of an excess of m-chlorobenzoic acid results in no observable ligand exchange. Addition of methanol to a dichloromethane solution of **1** results in only slight changes in the chemical shifts for **1**. If methanol is added to a dichloromethane solution containing both (N-MeTTP)Fe^{II}Cl and (N-MeTTP)Fe^{II}Br, ^{1}H NMR resonances of both components remain with only slight changes in their chemical shifts. We conclude that, in the solvents studied, these Fe^{II} complexes maintain a five-coordinate structure with one anionic axial ligand (halide, methoxide, etc.).

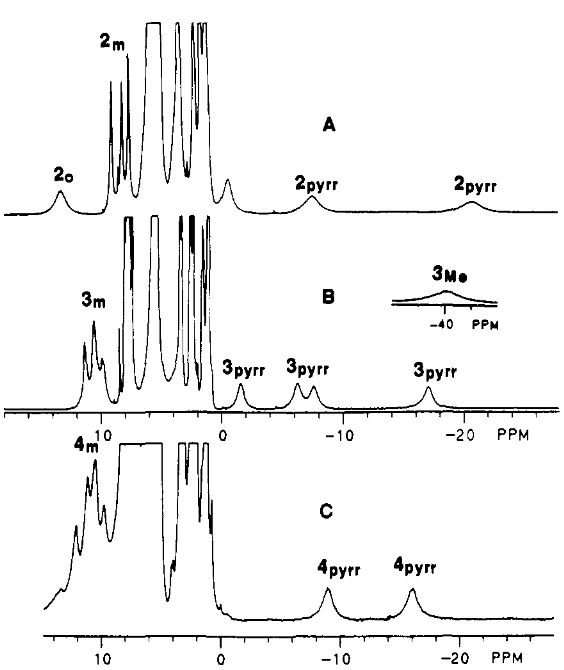

Figure 2. Trace A: Portion of the ^{1}H NMR spectrum of a sample of (N-MeTTP)Fe^{II}OCH$_3$ in dichloromethane-d_2/methanol-d_4 (4:1, v/v) at -90 °C in the presence of a 4-fold excess of sodium methoxide-d_3. Trace B: ^{1}H NMR spectrum recorded from the same sample after the addition of 1.1 equiv of m-chloroperoxybenzoic acid. The inset to trace B shows a broad resonance at ca. -40 ppm recorded with the sample warmed to -30 °C. This feature is not detectable when the sample is at -90 °C. Trace C: Sample of **3** after the addition of m-chlorobenzoic acid. Resonance assignments follow those in Figure 1 with resonances of (CD$_3$O)(N-MeTTP)Fe^{IV}=O labeled **3** and with m, the meta protons of the p-tolyl groups.

Oxidation of (N-MeTTP)Fe^{II}(OCD$_3$) (2) To Form the Fe(IV) Complex 3. Addition of m-chloroperoxybenzoic acid to a sample of (N-MeTTP)Fe^{II}(OCD$_3$) in the presence of excess sodium methoxide yields a new species, **3**. Figure 2 shows ^{1}H NMR spectral evidence of its formation. Trace A was obtained from a sample of (N-MeTTP)Fe^{II}(OCD$_3$), while trace B was obtained after adding 1.1 equiv of m-chloroperoxybenzoic acid. Four new resonances associated with a new species, **3**, are readily seen in the region 0 to -20 ppm. Observation of the ^{2}H NMR spectrum of a sample made from (N-{Me-d_3}TTP-pyrrole-d_8)Fe^{II}Cl allowed these four resonances to be assigned to the pyrrole protons. The N-methyl resonance is not observable at -90 °C because of its breadth, but it does become detectable when the sample is warmed. Three resonances in the 10–12 ppm range are assigned the meta protons of the p-tolyl groups on the basis of their intensities, multiplicities, and line widths. Attempts to synthesize **3** at higher temperatures results in considerable demetalation to yield N-MeTTPH. Once **3** is formed at -90 °C, however, it is stable to warming and can be observed at -20 °C where it suffers only slow decomposition. At room temperature demetalation is rapid.

Because of the thermal stability of **3**, it has been possible to monitor its ^{1}H NMR spectrum throughout the temperature range -90 to 0 °C. Plots of chemical shifts versus $1/T$ are given in Figure 3 for the four pyrrole resonances and one N-methyl resonance. These plots are linear as expected for a paramagnetic substance.

The transformation of **1** to **2** and then to **3** has also been monitored by electronic spectroscopy. The data are presented in Figure 4. The spectra obtained from **1** and **2** (traces A and B, respectively) are quite similar. Both show a split Soret peak that

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[27] Evans, D. F. *J. Chem. Soc.* **1959**, 2003.

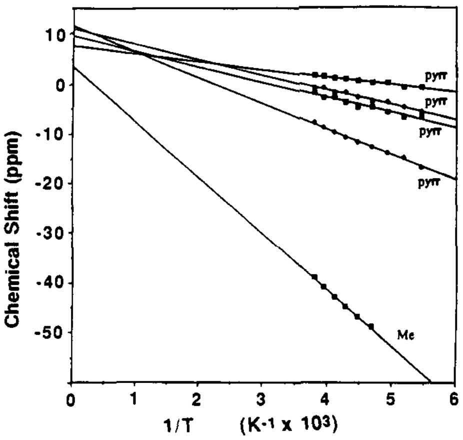


Figure 3. Plots of the chemical shifts versus $1/T$ for **3** in dichloromethane-d_2/methanol-d_4 (4:1, v/v).

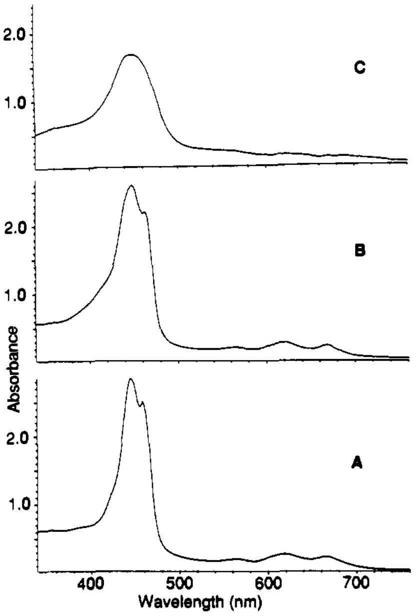


Figure 4. Electronic absorption spectra of dichloromethane/methanol (4:1, v/v) solutions: A, (*N*-MeTTP)$Fe^{II}Cl$ (**1**); B, (*N*-MeTTP)$Fe^{II}(OCH_3)$ (**2**) formed from **1** by the addition of sodium methoxide; C, (CH_3O)(*N*-MeTTP)$Fe^{IV}{=}O$ (**3**) formed from **2** by the addition of *m*-chloroperoxybenzoic acid. All spectra were recorded with the sample at -90 °C.

is characteristic of these five-coordinate complexes. The spectrum of **3** shows a typical porphyrin-type pattern with a broader Soret peak that is shifted to higher energy relative to **1** and **2**.

The magnetic susceptibility for **3** has been determined using the Evans technique.[27] The observed magnetic moment is 2.9 (3) μ_B over the temperature range -90 to -20 °C.

The formation of **3** in reproducible fashion requires the presence of a substantial excess of sodium methoxide which appears to provide an axial ligand. With less than a 4-fold excess of sodium methoxide, other species producing pyrrole resonances in the 0 to -20 ppm range are formed. One shows three equally intense pyrrole resonances at -2, -11, and -16 ppm while a second shows two equally intense pyrrole resonances at -9 and -16 ppm. These appear to involve coordination by different axial anionic ligands analogous to the Fe(II) experiment recorded in trace C of Figure 1.

Trace C of Figure 2 shows the ^1H NMR spectrum obtained after the addition of *m*-chlorobenzoic acid to a sample of **3**. The resonances of **3** have been replaced by those of a new but related species, **4**. This has two resonances in the 0 to -20 ppm region. The identity of these as two pyrrole resonances has been ascertained through ^2H NMR studies. When a corresponding sample is prepared from (*N*-MeTPP-pyrrole-d_8)$Fe^{II}Cl$, four ^2H NMR resonances due to the four pyrrole deuterons are observed at -10.8, -7.0, +0.33, and +2.5 ppm at -60 °C. Thus, in trace C, two pyrrole resonances are obscured by intense resonances in the diamagnetic envelope. Four resonances due to the meta phenyl protons are seen in trace C at 10-13 ppm. The resonance of the *N*-methyl group is not observable in the data of trace C. However, the ^2H NMR spectrum of a similarly prepared sample made from (*N*-{Me-d_3}TPP)$Fe^{II}Cl$ shows the *N*-Me resonance at -49.5 ppm at -60 °C. We suggest that **4** is obtained from **3** by replacement of an axial methoxide ligand by an axial *m*-chlorobenzoate ligand. Axial ligand resonances were not observed for **4**. Presumably they are located in the diamagnetic region of the spectrum.

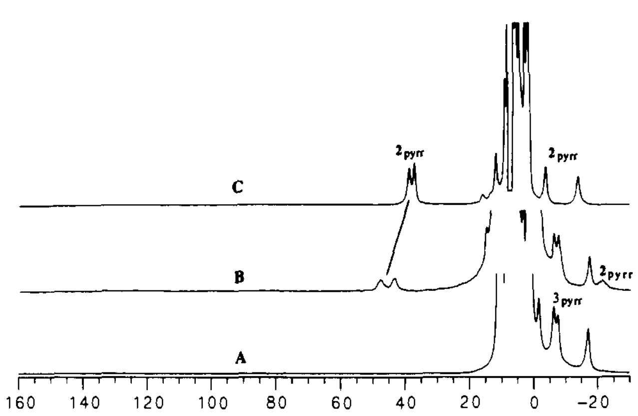


Figure 5. ^1H NMR spectra: A, **3** at -90 °C in dichloromethane-d_2/methanol-d_4 (4:1, v/v) with a 20-fold excess of sodium methoxide; B, same sample after the addition of 38 equiv of dimethylphenylphosphine; C, sample after warming to -30 °C.

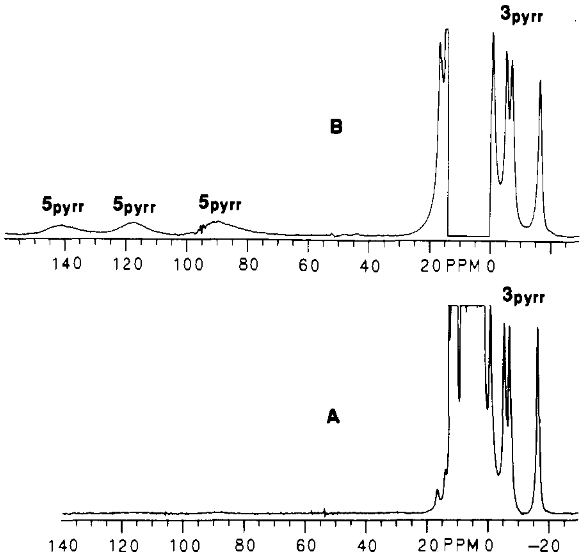


Figure 6. ^1H NMR spectra of a sample of **3** in 4:1 dichloromethane-d_2/methanol-d_4 at -90 °C: (A) before and (B) after the addition of 20 equiv of triphenylphosphine.

Reduction of 3. Compound **3** undergoes reduction when treated with tertiary phosphines. Figure 5 shows data concerning the reaction with dimethylphenylphosphine. Trace A shows the ^1H NMR spectrum of a sample of **3** at -90 °C prepared as described above except that a 20-fold excess of sodium methoxide is present. Trace B shows the ^1H NMR spectrum of the sample 30 min after the addition of a 38-fold excess of dimethylphenylphosphine. New resonances appear at 48, 43, and -22 ppm. These correspond to three of the four pyrrole resonances of (*N*-MeTTP)$Fe^{II}(OCD_3)$ (see Figure 1). Resonances of **3** are still apparent. On warming to -30 °C, however, the resonances of **3** decrease in intensity while those of (*N*-MeTTP)$Fe^{II}(OCD_3)$ increase as shown in trace C.

With triphenylphosphine and also with lower relative amounts of dimethylphenylphosphine, the reaction with **3** produces high-spin Fe^{III} complexes. Figure 6 shows relevant data. Trace A shows

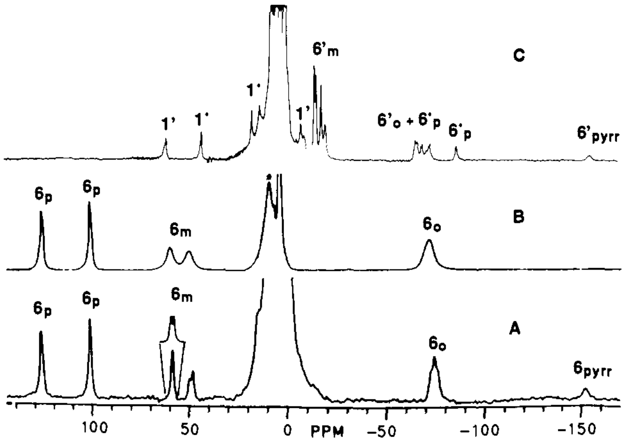


Figure 7. ^{1}H NMR spectra. (A) Solution of (N-MeTPP)Fe^{II}Cl in 3:1 dichloromethane-d_2/methanol-d_4 at −90 °C after the addition of a 10-fold excess of m-chloroperoxybenzoic acid. The resonances are due to **6**. (B) A similar solution of (N-MeT{T-d_7}P)Fe^{II}Cl in the presence of a 10-fold excess of m-chloroperoxybenzoic acid. (C) A similar solution of (N-MeT{3,5-Me$_2$C$_6$H$_3$}P)Fe^{II}Cl in the presence of a 10-fold excess of m-chloroperoxybenzoic acid. In trace C, resonances of unreacted (N-MeT{3,5-MeC$_6$H$_3$}P)Fe^{II}Cl are labeled 1′.

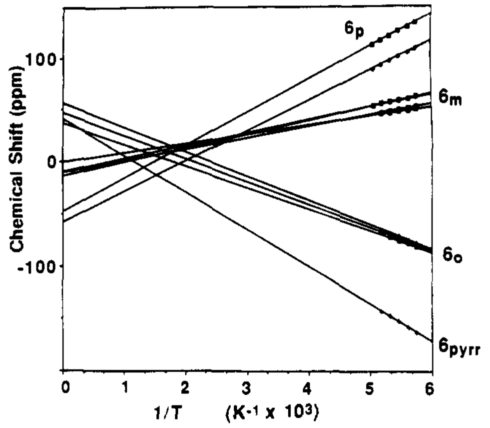


Figure 8. Plots of the chemical shift versus $1/T$ for **6** in dichloromethane-d_2/methanol-d_4 (4:1, v/v).

the spectrum of **3** obtained as previously described while trace B shows the sample after the addition of 20 equiv of triphenylphosphine. Three, new, broad resonances in the 90–150 ppm range are clearly discernable. These result from the formation of [(N-MeTTP)Fe^{III}X]$^+$ (**5**) (X = m-ClC$_6$H$_4$CO$_2^-$, OMe$^-$; the broad lines do not allow a distinction). The spectra of such high-spin complexes have been thoroughly analyzed earlier.[22] On warming, the resonances of **3** lose intensity while those of the Fe^{III} species grow. Resonances characteristic of (N-MeTTP)Fe^{II}(OCD$_3$) also can be observed. Notice that no high-spin Fe^{III} complex is present in the experiment presented in Figure 5, which is intentionally plotted so that the downfield region (where resonances of such a species should occur) is shown.

The differences between the course of the reaction shown in Figures 5 and 6 are accounted for by the observation that **3** reacts with **2** to also yield high-spin [(N-MeTTP)Fe^{III}X]$^+$ (**5**). At −90 °C addition of 0.5 equiv of m-chloroperoxybenzoic acid to a sample of (N-MeTTP)Fe^{II}(OCD$_3$) (**2**) yields an equimolar mixture of **2** and **3**. These react slowly at −90 °C but produce resonances characteritic of [(N-MeTTP)Fe^{III}X]$^+$ (X = m-ClC$_6$H$_4$CO$_2^-$, OMe$^-$) when warmed. Thus, when (N-MeTTP)Fe^{II}OCD$_3$ (**3**) is formed slowly (as occurs when small amounts of the more reactive dimethylphenylphosphine are used or whenever the less reactive triphenylphosphine is employed), it can react with **3** to form [(N-MeTTP)Fe^{III}X]$^+$. However, with a sufficient excess of the more reactive phosphine, dimethylphenylphosphine, it is possible to reduce **3** to **2** rapidly enough so that there is no reaction between **2** and **3**.

^{31}P NMR spectroscopy shows that the phosphine is converted into the corresponding phosphine oxide in the reductions of **3**. No other phosphorus-containing product is formed. In all cases the quantity of phosphine oxide produced was less than 1 equiv based on the quantity of **3** initially present. In control experiments, these phosphines do not react with [(N-MeTTP)Fe^{III}Cl]$^+$ in the presence of excess sodium methoxide to form any phosphine oxide.

Addition of m-Chloroperoxybenzoic Acid to (N-MeTTP)Fe^{II}Cl in the Absence of Methoxide. In the absence of sodium methoxide, the reaction between (N-MeTTP)Fe^{II}Cl and m-chloroperoxybenzoic acid takes different paths. When 1.1 equiv of the peroxyacid is added, the Fe^{II} complex is converted into a high-spin, five-coordinate Fe^{III} complex. However, when 5–10 equiv of peroxyacid is added, a new species with a remarkable ^{1}H NMR spectrum is produced. Relevant data are shown in Figure 7. Trace A shows the spectrum resulting from observation of a 4:1 dichloromethane-d_2/methanol-d_4 solution of (N-MeTTP)Fe^{II}Cl after the addition of 10 equiv of m-chloroperoxybenzoic acid. A new species, **6**, is present whose resonances extend from +130 to −160 ppm. The individual resonances have been assigned through labeling experiments and consideration of relative intensities. Trace B shows the ^{2}H NMR spectrum obtained under similar conditions from (N-MeT(T-d_7)P)Fe^{II}Cl. Five resonances are observed; the upfield resonance at −153 ppm in trace A is not present. Consequently, it is assigned to one of the four pairs of pyrrole protons. It is likely that the other pyrrole resonances occur under the diamagnetic envelope in the +15 to −5 ppm region. The five resonances seen in trace B result from the deuterated p-tolyl groups. The two equally intense resonances at 126 and 101 ppm can be assigned to the two types of p-methyl groups in the N-methylated porphyrin on the basis of their similar intensities and line widths. The other resonances are then due to the ortho and meta protons of the p-tolyl group. For an N-methyltetraarylporphyrin with C_s symmetry, there are four meta and four ortho phenyl environments. Notice that in trace A there are four distinct resonances in the 45–60 ppm region and that the resonance at ca. −75 ppm also shows multiplet character. Trace C shows the spectrum obtained by a comparable oxidation of (N-MeT(3,5-dimethylphenyl)P)Fe^{II}Cl. In comparison to trace A the two resonances at 126 and 101 ppm are absent as are the four resonances at 45–60 ppm. Consequently, the latter four resonances can be assigned to the meta protons of the p-tolyl group in **6**. The remaining set of resonances at ca. −75 ppm in trace A is therefore assigned to the ortho protons of **6**. Trace C shows a new group of four resonances of varying line widths but comparable intensities in the region of −10 to −20 ppm. These are assigned to the protons of the four meta methyl groups. A complex group of resonances appears in the −60 to −90 ppm region of trace C. These are due to para and ortho protons of the 3,5-dimethylphenyl group. The single peak at −155 ppm in trace C corresponds to a similar feature in trace A and is assigned to one pair of pyrrole protons.

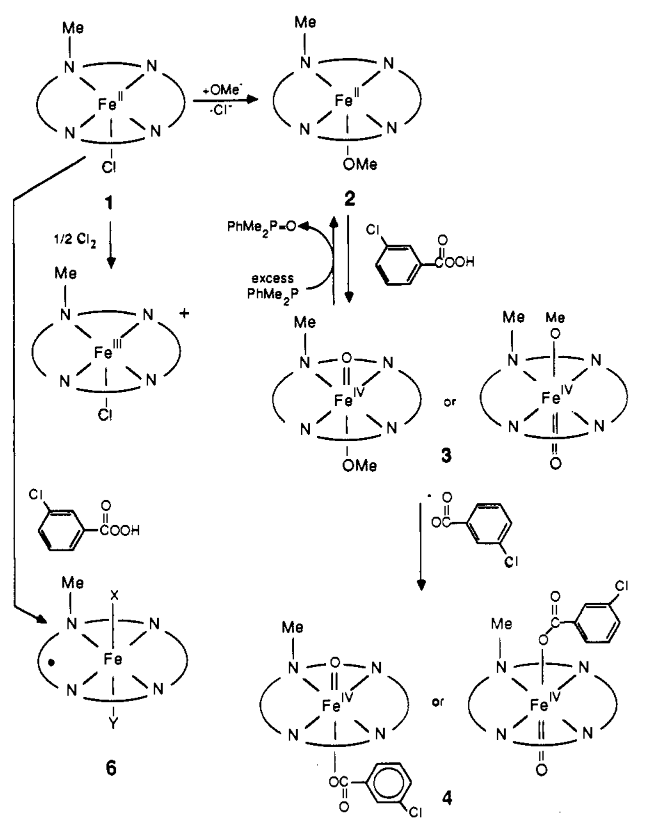
Species **6** can only be observed over the limited temperature range −99 to −75 °C. Above −75 °C it underoges decomposition. A plot of the chemical shifts versus $1/T$ reveals that all resonances seen for **6** show linear behavior over this small temperature range as seen Figure 8. However, the extrapolated shifts at infinite temperature deviate considerably from the anticipated diamagnetic positions.

No EPR signal was observed for **6** in samples that were frozen at 10 K. Only weak signals from a high-spin Fe^{III} impurity were observed at $g = 5.8$. The integrity of the sample used for this measurement was checked before and after the EPR measurement by ^{1}H NMR spectroscopy.

All preparations of **6** also show weak ^{1}H NMR resonances due to the presence of some **3**. While these are not readily visible in the spectra shown in Figure 6, careful inspection of the +10 to −20 ppm region shows that the appropriate resonances are present.

Methanol plays a critical role in stabilizing **6**. Treatment of (N-MeTTP)Fe^{II}Cl with 6 equiv of m-chloroperoxybenzoic acid in dichloromethane-d_2 alone results in oxidation to form a high-spin Fe^{III} complex and a species related to **3**. No resonances due to **6** can be detected. Addition of methanol at −90 °C results in the

Scheme I



complete conversion of the sample into **6**. Attempts to prepare **6** (and **3** also) using molecular chlorine, alkyl hydroperoxides, iodosylbenzene, and sodium hypochlorite as oxidants did not produce samples with NMR resonances characteristic of those species.

Reaction of (TMP)Fe^{II} with *m*-Chloroperoxybenzoic Acid. Since the reactivity of iron(II) porphyrins with the peroxyacid has not been previously described, this was examined. Treatment of (TMP)Fe^{II} in dichloromethane-d_2/methanol-d_4 (4:1, v/v) successively with sodium methoxide-d_3 and 1.1 equiv of *m*-chloroperoxybenzoic acid produced a red solution whose ^{1}H NMR spectrum (Table I) was consistent with the formation of $(CD_3O)(TMP)Fe^{IV} = O$. At −90 °C the pyrrole resonance is observed at −4.0 ppm. At −30 °C, this shifts to +0.1 ppm and two ortho and a single para methyl resonances are observed. The *m*-mesityl resonances are obscured by resonances of the *m*-chlorobenzoic acid that is produced. Plots of the chemical shifts versus $1/T$ for these resonances followed the Curie law. None of the resonances characteristic of $[(TMP^{\bullet})Fe^{IV}{=}O]^+$[13,14] were observed, even when an excess of peroxyacid was used in this reaction. These results demonstrate the ability of *m*-chloroperoxybenzoic acid to effect the oxidation of Fe^{II} to Fe^{IV}=O.

Discussion

Clearly, the most significant results reported here are the observations of the highly oxidized species **3**, **4**, and **6**. The reactions leading to these and other species described here are set out in Scheme I. The available data indicate that **3** is a complex of Fe(IV). The magnetic moment of 2.9 μ_B is consistent with the $S = 1$ ground state that is characteristic of d^4 complexes. Several iron(IV) porphyrin complexes have been previously characterized: the five and six-coordinate ferryl complexes (TMP)Fe^{IV}=O[28] and B(P)Fe^{IV}=O,[28-33] the methoxide complex (TMP)Fe^{IV}(OMe)$_2$,[34] and the phenyl complex (TTP)Fe^{IV}(Ph)Br.[35] Both (*N*-MeIm)(TmTP)Fe^{IV}=O and (TMP)Fe^{IV}(OMe)$_2$ have magnetic moments of 2.9 μ_B which do not vary with temperature over the range in which they are stable. (TPP)Fe^{IV}(C$_6$H$_4$CH$_3$-*p*)Br has a magnetic moment of 2.6 (4) μB.[35] The ^{1}H NMR spectral pattern observed for **3** is clearly distinct from those observed for high-spin Fe(II)[18] and high-spin Fe(III)[22] complexes of *N*-methylporphyrins. That pattern does, however, share similarities with the pattern reported for six-coordinate, low-spin iron(III) *N*-methylporphyrin complexes. Those similarities include upfield chemical shifts for both the pyrrole and *N*-methyl protons.[21] Nevertheless, the magnetic susceptibility of **3** rules out the possibility that it is a low-spin Fe^{III} complex which would have an $S = {}^1/_2$ ground state and a lower magnetic moment. Also, the average pyrrole chemical shift of **3** is considerably less than the average pyrrole chemical shift seen for low-spin Fe^{III} complexes such as [(*N*-MeTTP)Fe^{III}(*N*-MeIm)$_2$]$^+$ and [(*N*-MeTTP)Fe^{III}(CN)$_2$]$^-$.[21] However, the upfield *N*-methyl resonance shifts seen for both **3** and these low-spin Fe^{III} complexes appear to have a common origin that relates to their electronic structure. Large downfield shifts for the *N*-methyl group are seen for high-spin Fe^{II} (S = 2) and Fe^{III} ($S = {}^5/_2$) complexes of *N*-methylporphyrins.[18,21] These have the $d_{x^2-y^2}$ orbital half-occupied, and the resulting contact contribution produces a large downfield chemical shift for the *N*-methyl resonance. However, for low-spin Fe^{III} and for Fe^{IV}, the $d_{x^2-y^2}$ orbital is empty and this contact contribution is absent.

The average pyrrole chemical shift (−6.9 ppm at −80 °C) of **3** is also considerably lower than that seen for the Fe^{IV} complex (TMP)Fe(OCH$_3$)$_2$ (−37.5 ppm at −78 °C[34]). On the other hand, the pyrrole resonances for porphyrin ferryl complexes show relatively small hyperfine shifts and are dependent on the axial ligation. The small hyperfine shifts are consistent with molecular orbital calculations which indicate that the unpaired electrons in the ferryl group reside in strongly localized, π^* orbitals comprised of iron d_{xz} and d_{yz} and oxygen p_x and p_y orbitals.[36] The average pyrrole chemical shift seen for **3** is consistent with the presence of a ferryl unit. The NMR spectral patterns for **4** are similar to those of **3**. It is likely that the two differ in one axial ligand, with **3** having a methoxide and **4** a *m*-chlorobenzoate axial ligand.

The fact that **3** can be cleanly reduced back to **2** indicates that the basic *N*-methylporphyrin skeleton is preserved. The detection of phosphine oxides as products demonstrates the ability of **3** to act as an oxygen atom transfer agent. Such reactivity is not a property of the corresponding Fe^{III} complexes, since there is no reaction observed upon treating [(*N*-MeTTP)FeCl]$^+$ with tertiary phosphines under similar conditions. The ability of (*N*-MeIm)(TPP)Fe^{IV}=O to stoichiometrically oxidize triphenylphosphine to its oxide has been demonstrated previously.[30] The thermal stability of **3** is similar to that of (*N*-MeIm)(TPP)-Fe^{IV}=O.[29] The low reactivity of **3** toward phosphines suggests that **3** is not likely to be an effective agent for olefin epoxidation. However, in this context it should be noted that simple ferryl complexes like (*N*-MeIm)(TPP)Fe^{IV}=O also are not effective in the epoxidation of olefins.[37]

Taken as a whole, these results strongly suggest that **3** is a complex containing the ferryl, (Fe^{IV}=O)$^{2+}$, group with a methoxide ion acting as the other axial ligand (i.e., **3** is (CD$_3$O)(*N*-MeTTP)Fe^{IV}=O). This requires the iron to be six-coordinate,

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(28) Balch, A. L.; Chan, Y.-W.; Cheng, R.-J.; La Mar, G. N.; Latos-Grażyński, L.; Renner, M. W. *J. Am. Chem. Soc.* **1984**, *106*, 7779.

(29) Chin, D. H.; Balch, A. L.; La Mar, G. N. *J. Am. Chem. Soc.* **1980**, *102*, 1446.

(30) Chin, D. H.; La Mar, G. N.; Balch, A. L. *J. Am. Chem. Soc.* **1980**, *102*, 5945.

(31) La Mar, G. N.; de Ropp, J. S.; Latos-Grażyński, L.; Balch, A. L.; Johnson, R. B.; Smith, K. M.; Parish, D. W.; Cheng, R.-J. *J. Am. Chem. Soc.* **1983**, *105*, 782.

(32) Shin, K.; Goff, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 3140.

(33) Gold, A.; Jayaraj, K.; Doppelt, P.; Weiss, R.; Chottard, G.; Bill, E.; Ding, X.; Trautwein, A. X. *J. Am. Chem. Soc.* **1988**, *110*, 5756.

(34) Groves, J. T.; Quinn, R.; McMurray, T. J.; Nakamura, M.; Lang, G.; Boso, B. *J. Am. Chem. Soc.* **1985**, *107*, 354.

(35) Balch, A. L.; Renner, M. W. *J. Am. Chem. Soc.* **1986**, *108*, 2603.

(36) Hanson, L. K.; Chang, C. K.; Davis, M. S.; Fajer, J. *J. Am. Chem. Soc.* **1981**, *103*, 663.

(37) Arasasingham, R. D. Ph.D. Thesis, University of California, Davis, 1988. Traylor, T. G.; Fann, W.-P.; Bandyopadhyay. *J. Am. Chem. Soc.* **1989**, *111*, 8009.

a feature which we have shown recently is feasible for *N*-methylporphyrins despite the steric constraints imposed by the *N*-methyl group.[21] The closely related complex **4** is formulated as (m-$ClC_6H_4CO_2$)(*N*-MeTTP)Fe^{IV}=O. It is possible that the oxo group is proximal or distal to the *N*-methyl group as shown in the scheme. Arguments in favor of the proximal location include the availability of a vacant coordination site in **2** which can interact with the peroxyacid to form **3** directly and the limited tendency for **3** to react to form μ-oxo species.

Identification of the composition of **6**, the other type of oxidized complex described here, is more limited. This is largely because its low thermal stability allows us little opportunity to explore its chemical or physical properties. Moreover, the requirement that **6** be formed in the presence of a substantial excess of *m*-chloroperoxybenzoic acid severely limits any testing of the further reduction or oxidation reactions that might be associated with this species. Nevertheless, the ^1H NMR spectrum is informative about one aspect of its electronic structure. The sizable hyperfine shifts observed for the meso aryl substituents of the porphyrin along with the pattern of these shifts indicate that the *N*-methylporphyrin ligand has been oxidized to a porphyrin π radical (frequently referred to as a porphyrin π-cation radical). The alternating sign for the chemical shifts for the ortho and para aryl protons versus the meta aryl protons and the change in sign of the shift that occurs upon substituting a methyl group for a proton (or vice versa) are consistent with a π mechanism of spin delocalization into the meso aryl substituents from the meso carbon. Similar patterns have been seen for related porphyrin π radicals. The spectral pattern reported[38] for [(TPP$^\bullet$)$Fe^{III}(ClO_4)_2$] is very similar to that of **6**.

Although the precise locations of all of the pyrrole resonances of **6** are not known, the observation of one pyrrole resonance far upfield and the likelihood that the others are in the +15 to −5 ppm region are consistent with an electronic structure in which the $d_{x^2-y^2}$ orbital is not singly occupied.

This is the first case in which an *N*-methylporphyrin π radical has been unambiguously identified. The limited data do not give definitive information regarding the oxidation state of the iron or its axial ligation. Likely oxidation states for iron include Fe^{III} and Fe^{IV}. Available axial ligands are chloride, methoxide, and oxide.

In order to characterize the precursors to **3**, some further information on axial ligation in $Fe^{II}Cl$ complexes of *N*-methyltetra-*p*-tolylporphyrin was obtained. The reaction of sodium methoxide with (*N*-MeTTP)$Fe^{II}Cl$ results in the formation of a new high-spin iron(II) complex, (*N*-MeTTP)$Fe^{II}(OCH_3)$ (**2**). The NMR data and magnetic susceptibility are in accord with such a formulation. Previously, we have shown that substituted imidazoles and cyanide ion can also replace the axial chloride ligand in (*N*-MeTTP)$Fe^{II}Cl$.[18] Moreover, we have seen that changes in the axial ligands in these iron(II) complexes produce significant chemical shift variations.

The *p*-cresolate complex (*N*-MeTTP)$Fe^{II}(OC_6H_4CH_3$-*p*) shows axial phenolate resonances that are indicative of π-spin delocalization with ortho and meta protons showing shifts of opposite sign. The shift pattern is similar to that seen for aryloxy groups as axial ligands in high-spin Fe^{III} complexes, $PFe^{III}OAr$.[39]

Conclusions

The present work offers conclusive evidence that the *N*-methylporphyrin ligand can sustain (stabilize) highly oxidized forms of iron complexes. The evidence that **3** is an iron(IV) complex is compelling. Species **6** is clearly a complex that contains an *N*-methylporphyrin radical. Thus, this work presents the first spectroscopic identification of such a radical for the *N*-methylporphyrins. The formation of both **3** and **5** is critically dependent on the use of an oxygen atom source, *m*-chloroperoxybenzoic acid, for their formation. Molecular chlorine, ordinarily a potent oxidant, is not capable of forming either of these highly oxidized species. This work continues to emphasize the fact that *N*-methylporphyrins and normal porphyrins have similar abilities to stabilize corresponding spin/oxidation/ligation states of iron. The role of these oxidized species in olefin epoxidation remains to be explored. Nevertheless, their existence suggests that catalysis of epoxidation by N-substituted porphyrins follows a course similar to that observed with porphyrin catalysts. Finally, the observation of a ferryl complex with the *N*-methylporphyrin ligand forms a bridge between the intensively studied porphyrin systems and the developing area of non-heme iron catalyzed oxidations where evidence for the participation of ferryl intermediates is beginning to emerge.[40]

Experimental Section

Synthesis. All chemicals were purchased from Aldrich and used as received unless otherwise noted. *N*-MeTTPH, *N*-MeTTP(pyrrole-d_8)H, and *N*-MeTMPH were prepared by literature procedures.[41–43] *N*-MeT(*meso*-tolyl-d_7)PH was prepared by methylation of T(*meso*-tolyl-d_7)PH_2 which was in turn prepared by the condensation of pyrrole with tolualdehyde-d_8 by the Lindsay procedure.[43] *N*-MeT(3,5-dimethylphenyl)PH was prepared in an analogous manner.

Tolualdehyde-d_8. Tolualdehyde-d_8 was prepared by cerium(IV) oxidation of *p*-xylene-d_{10} according to Syper.[44] A 500-mL three-neck round-bottom flask was equipped with a magnetic stirrer and a side arm addition funnel and charged with 107 mL of 3.5 N HNO_3 and 2.5 g (0.022 mol) of *p*-xylene-d_{10}. The solution was stirred and warmed to approximately 60 °C. Diammoniohexanitratocerium(IV), $[(NH_4)_2(NO_3)_6Ce^{IV}]$ (52 g, 0.095 mol, 4.3 equiv), was dissolved in the addition funnel. The cerium solution was added at a rate such that the color of the reaction mixture was maintained between clear and light yellow-green (approximately 4 mL/min at the beginning of the reaction and less than 1 mL/min at the end of the reaction). After the addition of 255 mL of the cerium solution, the color no longer dissipated when the addition was interrupted. At this point the addition was stopped. The reaction was cooled to room temperature. The solution was extracted with methylene chloride (1 × 60 mL, 2 × 15 mL). The combined extracts were dried over $MgSO_4$, filtered, and distilled. The solvent was removed at atmospheric pressure. The product was distilled under vacuum (less that 1 Torr) at 53–54 °C to yield a pale yellow liquid (1.53 g, 54%). The above procedure was also used to prepare 3,5-dimethylbenzaldehyde from mesitylene.

Sodium Methoxide-d_3. Sodium was added to excess methanol-d_4 under dry N_2. After complete reaction, the salt was dried under vacuum.

***m*-Chloroperoxybenzoic Acid.** This was purchased as the 90% grade (balance *m*-chlorobenzoic acid) and standardized by iodometric titration according to Hiatt and co-workers.[45]

Preparation of 3. Five equivalents of $NaOCD_3$ (approximately 0.5 M in methanol-d_4) were added by microliter syringe to the NMR sample of (*N*-MeP)$Fe^{II}Cl$ (concentration 2–5 mM) at −90 °C (methanol slush bath). The sample was shaken in the cold bath, transferred to the NMR probe, and checked for conversion to (*N*-MeP)$Fe^{II}(OCD_3)$. *m*-Chloroperoxybenzoic acid (1.1 equiv, 0.5 M in CD_2Cl_2) was added by microliter syringe at −90 °C. The sample was mixed in the −90 °C bath and transferred to the NMR probe. Reactions of **3** were carried out by adding reagents (acids, ligands, reductants), as either a solution or a solid, to the cold sample of **3**.

Preparation of 5. Five to ten molar equivalents of *m*-chloroperoxybenzoic acid were dissolved in a minimum of methylene chloride, and the resultant solution was added in one portion to the NMR sample of (*N*-MeP)$Fe^{II}Cl$ at −90 °C. The solution was mixed in the −90 °C bath and transferred to the NMR probe.

Instrumentation. ^1H NMR were collected using a GE QE-300 or Nicolet NT-360 instrument operating at 300 or 360 MHz, respectively. A typical spectrum was collected over a 50000-Hz spectral window with 16K data points, 500–10000 transients per experiment, and a 50-ms prepulse delay. The free induction decay (FID) was appodized using an exponential multiplication which induced 10–200 Hz of line broadening. ^2H NMR were collected using a GE QE-300 or Nicolet NC-500 in-

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(38) Gans, P.; Buisson, G.; Duée, E.; Marchon, J.-C.; Erler, B. S.; Scholz, W. F.; Reed, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 1223.

(39) Arasasingham, R. D.; Balch, A. L.; Hart, R.; Latos-Grażyński, L.; *J. Am. Chem. Soc.* **1990**, *112*, 7566.

(40) Leising, R. A.; Brennan, B. A.; Que, L. A. Jr.; Fox, B. G.; Münck, E. *J. Am. Chem. Soc.* **1991**, *113*, 3988.

(41) Adler, A. D.; Longo, F. R.; Karplus, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443.

(42) Boersma, A. D.; Goff, H. M. *Inorg. Chem.* **1982**, *21*, 581.

(43) Lindsay, J. S.; Hsu, H. C.; Schreiman, I. C. *Tetrahedron Lett.* **1986**, 4969.

(44) Syper, L. *Tetrahedron Lett.* **1966**, *37*, 4493.

(45) Hiatt, R.; Mill, T.; Irwin, K. C.; Castleman, J. K. *J. Org. Chem.* **1968**, *33*, 1421.

strument at 46.1 or 76.8 MHz, respectively. A spectral width of 20 000 Hz was typical using 8K data points. A prepulse delay of 500 μs to 50 ms was used. Signal to noise was improved as described for the proton spectra. For samples with intense diamagnetic resonances a Super-WEFT pulse sequence[46] was used.

Electron paramagnetic resonance spectra were collected using a Bruker ER 200 D spectrometer and 4-mm-o.d. quartz sample tubes. The composition of the EPR samples was confirmed by placing the EPR sample tube into an NMR tube and collecting the NMR spectra before and after the EPR measurement.

Abbreviations used: P, porphyrin dianion; $P^{\bullet}$, porphyrin π radical monoanion; TPP, tetraphenylporphyrin dianion; TMP, tetramesitylporphyrin dianion; *N*-MeTTP, *N*-methyltetra-*p*-tolylporphyrin monoanion; *N*-MeIm, *N*-methylimidazole.

Acknowledgment. We thank the National Institutes of Health (Grant GM26226) for support.

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[46] Inubushi, T.; Becker, E. D. *J. Magn. Reson.* **1983**, *51*, 128.

Preparation and Characterization of Two New Group VI Quadruply Bonded Dinuclear Compounds: $Cr_2(DFM)_4$ and $W_2(DFM)_4$

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Abstract: Two new complexes, $Cr_2(DFM)_4$ (**1**) and $W_2(DFM)_4$ (**2**) (HDFM = di-*p*-tolylformamidine), have been synthesized to complete the triad of group VI dinuclear complexes with formamidine ligands. Direct interaction between $CrCl_2$ and LiDFM results in light yellow **1** (87%), which was crystallized as $Cr_2(DFM)_4{\cdot}2C_6H_6$ in space group *Pbnb* with $a = 17.021$ (3) Å, $b = 24.266$ (9) Å, $c = 15.335$ (3) Å, $V = 6334$ (3) Å^3, and $Z = 4$. The reaction between LiDFM and $Na_4(THF)_xW_2Cl_8$ affords orange **2**, which cocrystallizes with one toluene molecule in space group *P*4/*n* with $a = 13.259$ (2) Å, $c = 17.460$ (3) Å, $V = 3069$ (1) Å^3, and $Z = 2$. The metal–metal distances determined through diffraction study are 1.930 (2) and 2.187 (1) Å for **1** and **2**, respectively. While the cycle voltammogram of **1** is featureless within the range of +1500 to −2500 mV, a reversible oxidation for **2** was recorded at a potential of −280 mV, which suggests the accessibility of the $W_2(DFM)_4^+$ species. The magnetic anisotropies of several known $M_2(DFM)_4$ type compounds are estimated from their ^{1}H NMR data. The electronic spectra of both **1** and **2** have been explained on basis of the previous theoretical study on $Mo_2(DFM)_4$.

Introduction

In the development of the chemistry of multiply bonded dimetal compounds,[1] especially those with quadrupole bonds, it has always been of particular interest to obtain homologous series of compounds with metal atoms from the first, second, and third transition series embraced by the same set of ligands. To do this, bridging bidentate ligands (generally represented LL) have been especially useful. The first such series comprised the 2-oxo-6-methylpyridinato (mhp$^-$) compounds, $M_2(mhp)_4$, with M = Cr, Mo, and W,[2] and only in group VI have such homologous series been obtained. Despite their rarity, such series are of special importance because of the insight they can provide into the factors that control M–M multiple bond stability.

A class of LL ligands that have gradually become more important in preparing a wide variety of $M_2(LL)_4$ compounds are those of general type ArNXNAr$^-$, where Ar is either phenyl or *p*-tolyl (tol) and X is N or CH, and a considerable numbers of $M_2(ArNXNAr)_4$ compounds,[3-6] with the metals Ni, Ru, Os, Rh, Pd, and Ir have been synthesized and structurally characterized by employing the ligand [(tol)NCHN(tol)]$^-$, abbreviated DFM for ditolylformamidine. $Mo_2(DFM)_4$ is the only such compound well characterized among the group VI elements.[7] The dichromium complex with a ligand similar to DFM$^-$, $Cr_2[HC(N\text{-}3,5\text{-xylyl})_2]_4$, was synthesized earlier in a low yield (12%) by refluxing $Cr(CO)_6$ with neutral ligand for 18 days, but all attempts to grow suitable single crystals failed.[8] The molecular structure of the dichromium complex with another analogous ligand, *N*,*N*′-dimethylbenzamide, has also been determined, and this compound was one of the earliest examples of a "supershort" Cr–Cr bond (1.843 Å).[9]

Ditungsten complexes with metal–metal quadruple bonds are usually difficult to synthesize and manipulate, presumably because of the reactivity of the δ bond.[1b] The $W_2(LL)_4$ type complexes are only known for LL as carboxylates and hydroxypyridinate derivatives. Those ligands, as discussed in detail in the earlier studies of diruthenium(II) complexes, are relatively weak bases (poor in both σ and π donation). Hence, the isolation and characterization of a ditungsten(II) complex with a more basic ligand was considered a desirable objective in ditungsten chemistry.

In this report we describe the synthesis and molecular structure determination of both dichromium and ditungsten compounds with DFM. Some interesting spectroscopic and other physical properties will also be reported and discussed.

Experimental Section

All the syntheses and spectroscopic characterizations were carried out in argon atmosphere using standard Schlenkware. $CrCl_2$ was purchased

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[1] Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*, 2nd ed.; Wiley: New York, 1982.

[2] Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekustowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

[3] (a) Cotton, F. A.; Matusz, M.; Poli, R. *Inorg. Chem.* **1987**, *26*, 1472. (b) Cotton, F. A.; Matusz, M.; Poli, R.; Feng, X. *J. Am. Chem. Soc.* **1988**, *110*, 1144.

[4] (a) Cotton, F. A.; Ren, T. *Inorg. Chem.* **1991**, *30*, 3675. (b) Cotton, F. A.; Ren, T.; Eglin, J. L. *Inorg. Chem.* **1991**, *30*, 2559.

[5] Piraino, P.; Bruno, G.; Schiavo, S. L.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 2205.

[6] Cotton, F. A.; Poli, R. *Polyhedron* **1987**, *6*, 1625.

[7] Cotton, F. A.; Feng, X.; Matusz, M. *Inorg. Chem.* **1989**, *28*, 594.

[8] DerRoode, W. H.; Vrieze, K.; Koerner von Gustorf, E. A.; Ritter, A. *J. Organomet. Chem.* **1977**, *135*, 183.

[9] Bino, A.; Cotton, F. A.; Kaim, W. *Inorg. Chem.* **1979**, *18*, 1979.

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