Inorg. Chem. **2006**, *45*, 9742–9747

Inorganic Chemistry
Article

Iron Complexes of C- and N-Methylated 2-Aza-21-carbaporphyrin: NMR Studies

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Received June 17, 2006

Insertion of iron(II) into methylated derivatives of N-confused porphyrins 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-carbaporphyrin (*Me*CTPP*H*)H, 2-aza-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (CTPP*Me*)H$_2$, and 2-aza-2-methyl-5,10,15,20-tetraphenyl-21-methyl-21-carbaporphyrin (*Me*CTPP*Me*)H yielded N- or C-methylated high-spin iron(II) complexes (*Me*CTPP*H*)Fe^{II}Br, (*H*CTPP*Me*)Fe^{II}Br, and (*Me*CTPP*Me*)Fe^{II}Br. One electron oxidation of (*Me*CTPP*H*)Fe^{II}Br using Br$_2$, accompanied by deprotonation of a C(21)–H(21) fragment and formation of an Fe–C(21) bond, produces an intermediate-spin, five-coordinate iron(III) complex (*Me*CTPP)Fe^{III}Br. Simultaneously, a high-spin complex [(*Me*CTPP*H*)Fe^{III}Br]$^+$ was formed which preserved the side-on interaction between the metal ion and the inverted pyrrole ring. [(*Me*CTPP*H*)Fe^{III}Br]$^+$ was also obtained by titration of (*Me*CTPP)Fe^{III}Br with TFA due to the C(21) protonation. A titration of (*H*CTPP*Me*)Fe^{II}Br and (*Me*CTPP*Me*)Fe^{II}Br with Br$_2$ yielded solely corresponding high-spin iron(III) species [(*H*CTPP*Me*)Fe^{III}Br]$^+$ and [(*Me*CTPP*Me*)Fe^{III}Br]$^+$. Dioxygen reacts cleanly with (*Me*CTPP*H*)-Fe^{II}Br carbaporphyrin to form solely (*Me*CTPP)Fe^{III}Br. The ^{1}H NMR spectra of paramagnetic iron(II) and iron(III) complexes were examined. The characteristic patterns of pyrrole, *C*-methyl, and *N*-methyl resonances were found diagnostic of the ground electronic state of iron and the coordinating nature of the N-confused pyrrole. The characteristic C–*Me* resonances occur in a unique window (520–420 ppm) for iron(III) C-methylated N-confused porphyrins which remains in contrast with relatively small values found for iron(II) C-methylated derivatives (50–80 ppm).

Introduction

Carbaporphyrinoids are versatile ligands that offer a suitable platform to study the metal−carbon bond or interaction in a macrocyclic environment.[1−4] The coordination brings the metal ion into the vicinity of the embedded arene leading to activation of C−H bonds followed by dissociation and coordination or weak interactions, which can be spectroscopically observed.[2,5−10] The first discovered carbaporphyrinoid, N-confused (inverted) porphyrin,[11,12] and its derivatives revealed a remarkable tendency to stabilize unique organometallic compounds.[3,13−17] The dimeric or oligomeric structures involving N-confused porphyrins linked by external coordination using the N(2) donor attract particular interest.[17−24]

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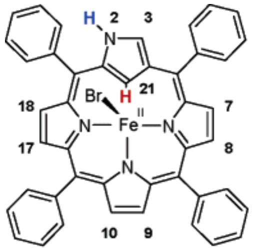
Chart 1. Iron(II) 2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrin



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The coordination chemistry of carbaporphyrinoid complexes of iron has been originally explored for iron(II) and iron(III) complexes.[5,6,19,25−27] Thus, iron(II) N-confused porphyrin complexes (*H*CTPP*H*)Fe^{II}Br (**1**) (Chart 1)[28] present the structure with the side-on position of the iron with respect to the inverted pyrrole plane.[25] Subsequently, a dimeric iron(II) N-confused porphyrin, $[(CTPPH)Fe^{II}]_2$, was obtained.[19] Similarly as for **1**, the side-on coordination mode has been determined for iron(II) *meta*-benziporphyrin.[5] Under aerobic conditions (*H*CTPP*H*)Fe^{II}Br transforms into a μ-hydroxo-bridged iron(III) dimer, $[(CTPPO)Fe^{III}]_2OH\cdot Na(THF)_2$. Oxygenation occurred at the inner core pyrrolic carbon yielding a tranformed $(CTPPOH)H_2$ porphyrinic ring.[19] Recently it was also demonstrated that the iron(III) N-confused porphyrin complex assembled using axially coordinated phenol and the perimeter nitrogen of the macrocycle.[26] Oxidation and oxygenation of **1** were systematically investigated using ^1H and ^2H NMR spectroscopy.[27] Two modes of coordination of iron(III) to the N-confused pyrrole ring (side-on and via trigonally hybridized carbon atom) were determined. In the presence of oxygen the formation of the C(21)═O carbonyl group was established which was involved in a direct interaction between the iron center and the π electron density on the carbonyl group in an η^2 mode.

Taking advantage of the unusual reactivity of N-confused porphyrin and its nickel(II) complex, the group of N-confused porphyrins has been extended using the alkylation procedure, yielding N- and/or C-methylated N-confused porphyrins.[29−33] The present contribution describes the synthesis of N- or C-methylated high-spin iron(II) complexes (*Me*-CTPP*H*)Fe^{II}Br (**2**), (*H*CTPP*Me*)Fe^{II}Br (**3**), and (*Me*CTPP*Me*)Fe^{II}Br (**4**) (Chart 2).

As a part of our continuing program of investigating the general relationship between the isotropic shift pattern and the molecular and electronic structures of paramagnetic carbaporphyrinoids, we have concentrated on examining ^1H NMR spectra as a source of insight into the electronic and molecular structure of the low-symmetry iron(II) carbaporphyrinoids and their oxidation products. The introduction of the methyl group(s) to the initial (*H*CTPP*H*)Fe^{II}Br (**1**) is expected to shape the reactivity of the resulting iron(II) complexes. Consequently, the reactivity of **2**−**4** allows us to elucidate influence of methylation.

Results and Discussion

NMR of Iron(*n*) N-Confused Porphyrin. The ^1H NMR data for paramagnetic iron(*n*) N-confused porphyrins have been analyzed considering their C_1 symmetry, determined previously in the crystal structure of (*H*CTPP*H*)Fe^{II}Br (**1**).[25] There are seven distinct β-H pyrrole positions for the **1**−**4** species, a 2-NH position for **3**, analogous to 2-CH of the regular porphyrin, and four different meso sites. Respective ^1H NMR spectra for (*Me*CTPP*H*)Fe^{II}Br (**2**), (*H*CTPP*Me*)Fe^{II}Br (**3**), and (*Me*CTPP*Me*)Fe^{II}Br are presented in Figure 1. The NMR data for oxidation products are presented in Figures 2 and 3. The spectral parameters have been gathered in Table 1. Resonance assignments, which are given above selected peaks, have been made on the basis of relative intensities and line widths. We have readily found that there is considerable analogy in ^1H NMR properties within each iron(*n*) N-confused porphyrin−iron(*n*) methylated N-confused porphyrin pair. Actually this follows the parallel that has been drawn between iron 21-heteroporphyrin and iron *N*-methylporphyrins.[13,34,35] Thus, our major assignment effort has been focused on the N−*Me* and C−*Me* resonances as they provide the essentially new insight into the electronic structure of the formed species. The unique relative intensity of the C−*Me* and N−*Me* resonances corresponding to three hydrogens afforded readily their unambiguous assignments. The plots of the temperature dependence of the chemical shifts which are typical for given electronic state of iron inverted porphyrin are shown in the Supporting Information (Figures 1S−5S).

^{1}H NMR of Iron(II) Methylated N-Confused Porphyrin. The ^1H NMR spectrum of (*Me*CTPP*H*)Fe^{II}Br (**2**) bears substantial similarities to the spectrum of **1**[6,27] and in more general terms to the spectra of high-spin iron(II) core modified porphyrins.[34,36,37]

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(28) We will use the symbol CTPP to denote the trianion obtained from the inverted porphyrin by abstraction of all pyrrolic NH proton and the C-bound H(21) hydrogen. The groups attached to the N(2) atom will be indicated by a prefix in italic, and the group attached to C(21) will appear as a suffix in italic. A similar methods will be used to form acronyms for other carbaporphynoids.

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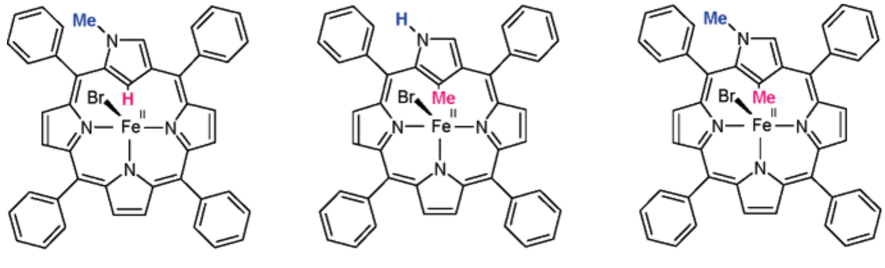
Chart 2. Iron(II) C- and/or N-Methylated 2-Aza-5,10,15,20-tetraphenyl-21-carbaporphyrins



2 **3** **4**

Five pyrrole resonances of (*Me*CTPP*H*)Fe^{II}Br (**2**) are spread out at the low-field region from 30 to 50 ppm with chemical shifts of 49.2, 48.3, 42.6, 39.7, and 34.1 ppm (298 K). Two other β-H resonances in analogy to **1** occur in the crowded 0−10 ppm region. The additional resonances, presented in Figure 1 in the 15−0 ppm range, are assigned to the *meso*-phenyl hydrogens. The most characteristic ^{1}H NMR feature (*Me*CTPP*H*)Fe^{II}Br (**2**), i.e., the remarkably downfield-shifted resonance at 653 ppm (line width 3750 Hz, at 293 K, dichloromethane-d_2), has been assigned to the internal H(21) hydrogen. The corresponding H(21) resonance of **1** was previously located at 812 ppm (line width 6200 Hz, at 293 K, dichloromethane-d_2).[6] The N−*Me* resonance has been identified at 59.3 ppm as distinguished by its characteristic three hydrogen intensity. The resonance assignments of (*H*CTPP*Me*)Fe^{II}Br (**3**) resemble those of **2**. The C−*Me* resonance at 85.6 ppm (293 K) has been readily identified since it is missing in the spectra **1** and **2** (Figure 1, Table 1). Two resonances of the N-confused pyrrole ring (2-NH and H(3)) have been located at 0.45 and 1.7 ppm. The dimethylated species **4** combines the features of two monomethylated counterparts albeit the downfield isotropic shifts of N−*Me* and C−*Me* are significantly smaller than those determined for **2** (N−*Me*) and **3** (C−*Me*), respectively (trace C in Figure 1, Table 1). For the sake of comparison the relevant paramagnetic shifts determined previously for analogous nickel(II) complexes i.e., (*H*CTPP*Me*)Ni^{II}Cl and (*Me*CTPP*Me*)Ni^{II}Cl, have been also included in Table 1.[30] The noticeable similarities of the spectroscopic patterns including the downfield positions of C−*Me* resonances suggest that for both cases the isotropic shift is dominated by similar mechanisms. The paramagnetic shifts of high-spin iron(II) N-confused porphyrin **1** and its methylated derivatives (**2**−**4**) can be explained by a model typically applied to high-spin iron(II) porphyrins and iron(II) *N*-substituted porphyrins.[38] In the case of a high-spin iron(II) center—$(d_{xy})^2(d_{xz}d_{yz})^2(d_{z^2})^1(d_{x^2-y^2})^1$—both σ and π routes of spin density delocalization can operate. The contact shift

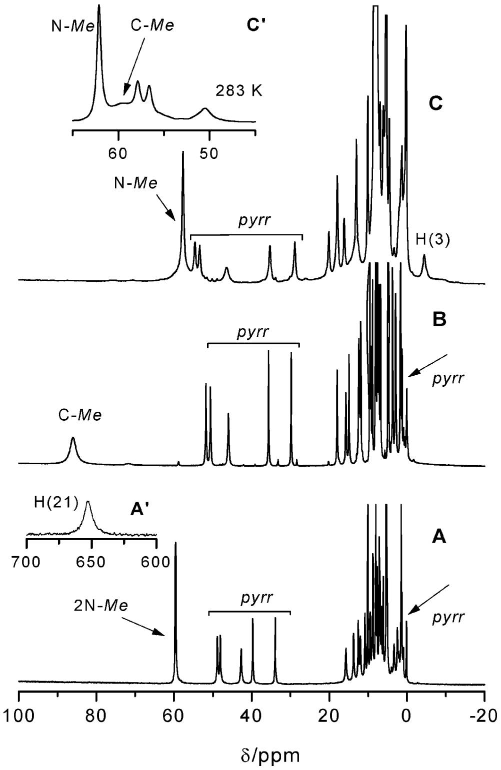


Figure 1. ^{1}H NMR spectra of iron N-confused porphyrins: A, (*Me*CTPP*H*)Fe^{II}Br (**2**); B, (*H*CTPP*Me*)Fe^{II}Br (**3**); C, (*Me*CTPP*Me*)Fe^{II}Br (**4**) (inset C′, 283 K). All spectra were collected in dichloromethane-d_2 at 298 K.

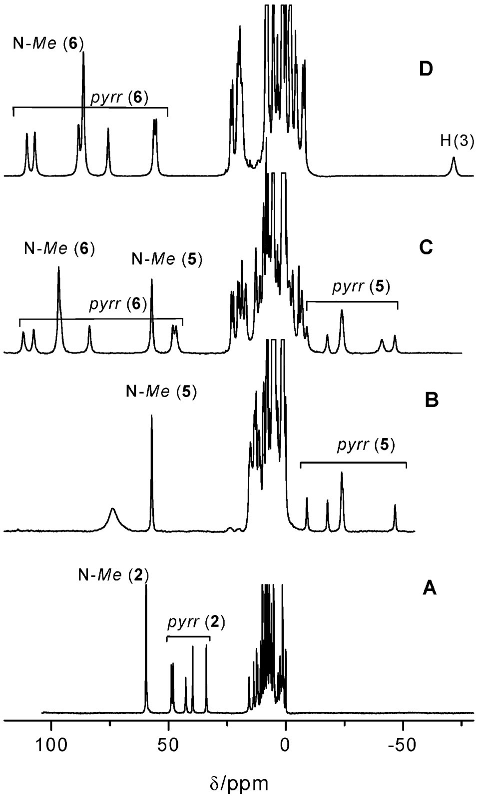


Figure 2. ^{1}H NMR spectra of [(*Me*CTPP*H*)Fe^{II}Br] (**2**) (dichloromethane-d_2, 298 K) after addition of Br$_2$: A, 0 equiv; B, 1 equiv; C, 2 equiv; D, 3 equiv. The peak labels refer to pyrrole resonances of dominating species as follows: B, [(*Me*CTPP)Fe^{III}Br] (**5**); D, (*Me*CTPP*H*)Fe^{III}Br (**6**).

Table 1. ^{1}H NMR Chemical Shifts of Iron C- and N-Methylated 2-Aza-21-carbaporphyrins[a]

compd	pyrrole[b]	H(21)	2-N−*Me*	C(21)−*Me*
(*Me*CTPP*H*)Fe$^{\mathrm{II}}$Br (**2**)	49.2, 48.3, 42.6, 39.7, 34.1	653	59.3	
(*H*CTPP*Me*)Fe$^{\mathrm{II}}$Br (**3**)	52.7, 51.9, 46.6, 36.6, 30.5, 1.7,[c] 0.5[c]			85.6
(*Me*CTPPMe)Fe$^{\mathrm{II}}$Br (**4**)	54.7, 53.4, 46.2, 34.9, 28.5, −4.3		57.8	57
[(*Me*CTPP*H*)Fe$^{\mathrm{III}}$Br]$^+$ (**6**)	110.4, 107.1, 88.3, 75.9, 57.0, 55.3, −71.6		87.10	
[(*H*CTPP*Me*)Fe$^{\mathrm{III}}$Br]$^+$ (**7**)	116.2, 112.3, 97.8, 84.1, 51.2, 37.4, −51.8,[c] −60.7[c]			498.5
[(*Me*CTPP*Me*)Fe$^{\mathrm{III}}$Br]$^+$ (**8**)	113.7, 112.9, 95.2, 81.6, 47.6, 46.2, −75.3[d]		100.5	431.9
(*Me*CTPP)Fe$^{\mathrm{III}}$Br (**5**)	−9.1, −17.8, −23.7, −23.9, −24.4, −46.7		57.36	
(*H*CTPP*H*)Fe$^{\mathrm{II}}$Br[6]	44.8, 43.7, 43.7, 31.7, 31.7, 8.4, 0.78, −8.0[e]	812		
[(*H*CTPP*H*)Fe$^{\mathrm{III}}$Br]$^+$ [27]	115.2, 112.9, 107.9, 91.5, 50.7, 35.9, −32.8,[d] −31.2[e]			
(*H*CTPP)Fe$^{\mathrm{III}}$Br[27]	7.2, −10.6, −19.2, −20.6, −23.2, −24.9, −43.2, −76.6[e]			
(TPP-N*Me*)Fe$^{\mathrm{II}}$Cl][34]	46.4, 32.4, 3.0, 0.11			92[f]
[(TPP-N*Me*)Fe$^{\mathrm{III}}$Cl]$^+$ [g,35]	128, 92, 79			272[f]
*(H*CTPP*Me*)Ni$^{\mathrm{II}}$Cl[30]	58.1, 58.1, 52.4, 48.2, 26.5, 24.9, 2.04, −23.07[e]			109.7
*(Me*CTPP*Me*)Ni$^{\mathrm{II}}$Cl[30]	58.8, 55.4, 50.1, 47.9, 24.2, 23.9, −1.7		32.5	117.4

[a] δ/ppm, at 298 K unless marked differently. [b] Includes resonances β-H, 2-NH, and H(3) of the N-confused pyrrole ring. [c] 2-NH or H(3) of the N-confused pyrrole ring. [d] H(3) of the N-confused pyrrole ring. [e] 2-NH of the N-confused pyrrole ring. [f] The resonance of N(21)*Me*. [g] At 223 K.

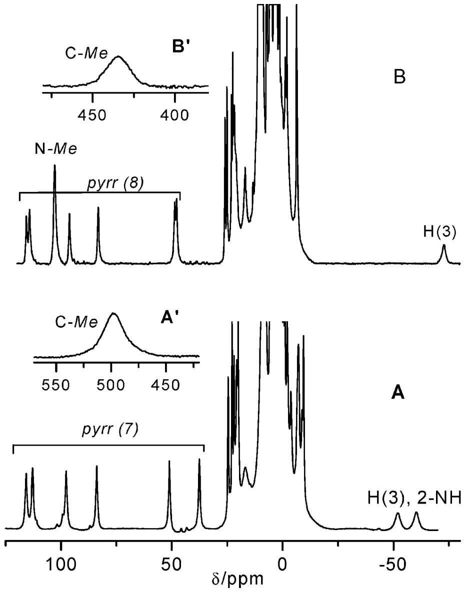


Figure 3. ^{1}H NMR spectra of A, [(*H*CTPP*Me*)Fe$^{\mathrm{III}}$Br]$^+$ (**7**), and B, [(*Me*CTPP*Me*)Fe$^{\mathrm{III}}$Br]$^+$ (**8**) (dichloromethane-d_2, 298 K). The insets present the strong downfield-shifted C−*Me* resonances.

predominates for the regular pyrrole resonances yielding their downfield positions.[34,37,38] The typical delocalization pathways involve the delocalization through a σ-framework by way of a σ-donation to the half-occupied $d_{x^2-y^2}$ iron(II) orbital.[34] Actually the variation of the β-H positions in the ^{1}H NMR spectrum may be accounted for by specific π-delocalization mechanisms discussed in detail for iron(III) porphyrins.[39,40] The spectroscopic distinctive feature of the iron(II) N-confused porphyrins **1**−**4** is the localized effect of the N-confused pyrrole ring. In the case of **1** and **3**, H(3) and 2-NH resonances are evidently different from the other six and show upfield positions. The logical conclusion that follows is the side-on location of the iron(II) with respect to the pyrrole ring primarily affects spin transfer to the modified pyrrole ring. The analogous effect has been observed for paramagnetic nickel(II) 2-aza-21-carbaporphyrin and metalloheteroporphyrins.[13,30] The uniquely large isotropic shift of the inner H(21) hydrogen determined for **2** indicates an Fe$^{\mathrm{II}}$−{C(21)−H} agostic interaction similarly as previously determined for **1**.[6] There the peculiar metal ion−inverted pyrrole ring interaction detected in the solid-state structure of (*H*CTPP*H*)Fe$^{\mathrm{II}}$Br (**1**) has been clearly reflected by an extremely large isotropic shift of the engaged H(21) atom (Table 1).[25]

The isotropic shift of the inverted C-methylated pyrrole ring is of a significant importance considering the nature of the interaction in this paramagnetic organometallic high spin iron(II) complex and requires a special comment. The considerable downfield C−*Me* shift can be accounted for by the delocalization in the Fe···(21)−C−H fragment. The direction and magnitude of the shifts are close to those reported for the N−*Me* group of the high-spin iron(II) *N*-methylporphyrin complex (TPP−N*Me*)Fe$^{\mathrm{II}}$Cl where the σ-delocalization operates via the Fe−N−C−H route.[34] The tilt of the inverted C-methylated ring changes the geometry of the spin density delocalization as compared to the regular pyrrole rings allowing the Fe···C(21)−C−H route. The unpaired spin density is localized on the molecular orbital dominated by the p_z component, which can transfer the σ-spin density but simultaneously contributes to π-orbitals of the inverted pyrrole ring. Such an overlap within the inverted ring will permit the direct transfer of unpaired spin density of the C(21) p_z orbital into the π system without any π M−L bonding.[41] The replacement of the upfield-shifted 2-NH proton of **1** with the methyl group of **2** or **4** results in the downfield shift of N−*Me*. This fact demonstrates a contribution of the π-transfer mechanism at this fragment of C-methylated iron(II) carbaporphyrin.

Reaction of (*Me*CTPP)Fe$^{\mathrm{II}}$Br with Bromine. A careful titration of (*Me*CTPP*H*)Fe$^{\mathrm{II}}$Br (**2**) with Br_2 has been carried out in strictly anaerobic conditions. The effect of addition 1 equiv of bromine to a solution of (*Me*CTPP*H*)Fe$^{\mathrm{II}}$Br (**2**) is shown in the ^{1}H NMR spectrum trace B of Figure 2.

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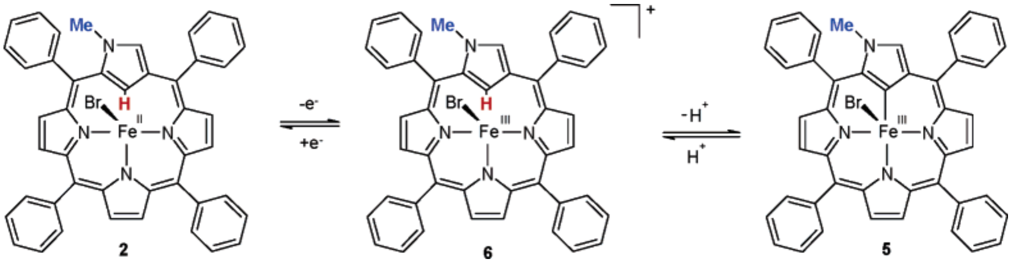
Scheme 1. Oxidation of **2**



Initially the resonances of (*Me*CTPP*H*)Fe^{II}Br (Figure 2, trace A) have decreased in intensity and new resonances, assigned as (*Me*CTPP)Fe^{III}Br (**5**), have grown gradually (Figure 2, trace B). The spectral changes, similar to those shown in Figure 2, have also been detected when dioxygen has been added to the solution of (*Me*CTPP*H*)Fe^{II}Br (see below). The pyrrole resonances of **5** are spread in the upfield from region −9.1 to −60.0 ppm (298 K, dichloromethane-d_2). The most downfield single resonance at 57.4 ppm has been identified as corresponding to the N−*Me* group. The peculiar spectroscopic pattern resembling one detected previously for (*H*CTPP)Fe^{III}Br (Table 1)[27] is consistent with formation of the five-coordinate (*Me*CTPP)Fe^{III}Br species where all internal donors including the trigonally hybridized C(21) atom are involved in regular coordination. The signs and magnitudes of the isotropic shifts of **5** are consistent with such a intermediate-spin ground electronic state.[27,42,43] As expected for the π-delocalization mechanism the strongly upfield shifted 2-NH resonance of (*H*CTPP)Fe^{III}Br has been replaced in (*Me*CTPP)Fe^{III}Br by the downfield one of N−Me.[38] Simultaneous broadening of (*Me*CTPP*H*)Fe^{II}Br resonances and their gradual relocation in the course of titration have also been noticed. Eventually, the originally broadened lines, resembling the spectrum of (*Me*CTPP*H*)-Fe^{II}Br, transform into the characteristic set of resonances assigned to [(*Me*CTPP*H*)Fe^{III}Br]$^+$ (**6**) (Figure 2, trace D), i.e., to the product of one-electron, metal-centered oxidation of **2**. Thus, in the course of this one-electron oxidation two iron(III) products **5** and **6** have been formed as accounted for by the ^{1}H NMR spectrum (Scheme 1). Separate resonances of (*Me*CTPP*H*)Fe^{II}Br (**2**) and [(*Me*CTPP*H*)Fe^{III}Br]$^+$ (**6**) could not be detected in the course of titration with bromine (Figure 2, trace B). Instead an averaged pattern has been observed. Thus, the rate of electron exchange between these two species is fast on the ^{1}H NMR time scale suggesting that relatively modest structural changes occur in the course of the redox process.

The pyrrole resonances of [(*Me*CTPP*H*)Fe^{III}Br]$^+$ (**6**) are spread in the 100 to −40 ppm region reflecting the intrinsic asymmetry of the ligand and the high-spin state of the metal ion. The most upfield resonances has been identified as corresponding to H(3) as the peculiar upfield position of these resonances may reflect the specific location of the inverted pyrrole with respect to the metal ion.[30] An effort has been made to locate the H(21) resonance of [(*Me*CTPP*H*)Fe^{III}-Br]$^+$ similarly as it has been done for **1** or **2**. The substantially larger broadening of all perimeter β-H pyrrole resonances has been seen for [(*Me*CTPP*H*)Fe^{III}Br]$^+$ (**6**) in comparison to (*Me*CTPP*H*)Fe^{II}Br (**2**). Presuming that the similar relation of line widths due to the analogous structures and mechanisms of spin delocalization holds for the H(21) position for [(*Me*CTPP*H*)Fe^{III}Br]$^+$ (**6**) and (*Me*CTPP*H*)Fe^{II}Br (**2**), the predicted line width of H(21) is well in excess of reasonably observed lines in the conditions of our experiment.

The process of one-electron oxidation is likely to proceed as shown in Scheme 1. Depending on the choice of oxidizing agent, a preference for **6** (Br_2) or **5** (O_2) has been observed. Thus is the course of oxidation with Br_2; two iron(III) inverted porphyrin complexes (**5** and **6**) remained in the detected acid−base equilibrium in the presence of iron(II) complex. The species **5,** once exclusively formed with dioxygen, could be converted into **6** by addition of trifluoroacetic acid. A titration of (*H*CTPP*Me*)Fe^{II}Br (**3**) and (*Me*CTPP*Me*)Fe^{II}Br (**4**) with Br_2 yielded solely corresponding high-spin iron(III) species [(*H*CTPP*Me*)Fe^{III}Br]$^+$ (**7**) and [(*Me*CTPP*Me*)Fe^{III}Br]$^+$ (**8**) (Figure 3). Clearly, the C-methylation blocks an access to the anionic σ-coordination of C(21).

Both species demonstrate a spectroscopic pattern of pyrrole resonances which is characteristic for high-spin iron(III) N-confused porphyrins exemplified by [(*H*CTPP*H*)Fe^{III}Br]$^+$ (Table 1).[27] The most characteristic ^{1}H NMR features of [(*H*CTPP*Me*)Fe^{III}Br]$^+$ (**7**) and [(*Me*CTPP*Me*)Fe^{III}Br]$^+$ (**8**), i.e the broad resonances at 498 ppm for **7** or 432 ppm for **8**, have been assigned to the internal C−*Me* groups (Figure 3). The enormous downfield C−*Me* shift can be accounted for by the delocalization in the Fe···C(21)−C−H fragment. The directions and magnitudes of the shifts resemble those reported for the N−*Me* group of the [(*Me*TPP)Fe^{III}Cl]$^+$ complex.[35]

Reaction with Dioxygen. Addition of dioxygen to dichloromethane-d_2 solution of (*Me*CTPP*H*)Fe^{II}Br (**2**) produces marked changes in ^{1}H NMR spectra. The resonances of (*Me*CTPP*H*)Fe^{II}Br have decreased in intensity, and new resonances, assigned to (*Me*CTPP)Fe^{III}Br (**5**), have grown gradually. The total and selective conversion of **2** to **5** requires 1 h at 298 K, thus only slightly slower as detected previously for **1**. The further exposition of the sample for dioxygen even for 12 days did not resulted in insertion of oxygen atom into the preformed Fe−C(21) bond as was previously detected for nonmethylated analogues.[27] The

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(42) Rachlewicz, K.; Latos-Grażyński, L.; Vogel, E.; Ciunik, Z.; Jerzykiewicz, L. *Inorg. Chem.* **2002**, *41*, 1979.

(43) Ohgo, Y.; Neya, S.; Ikeue, T.; Takahashi, M.; Takeda, M.; Funasaki, N.; Nakamura, M. *Inorg. Chem.* **2002**, *41*, 4627.

exposition of **4** toward air results in formation of high-spin species **8**, but the process requires several days.

Conclusion

This work broads our understanding of the coordination of iron in an N-confused porphyrin environment. It serves to establish the similarities of iron(*n*) N-confused and C- and N-methylated N-confused porphyrin complexes for a given oxidation/spin state. Within each of these pairs there is considerable analogy in ^{1}H NMR properties. The analytically useful hyperfine shift patterns, determined previously for iron(II) and iron(III) N-confused porphyrins, provided useful and potentially unique probes for detecting the analogous species by ^{1}H NMR spectroscopy. This spectroscopic means of identification has gained an essential addition. Namely, the characteristic large downfield C−*Me* contact shift provides a well-defined signal in a unique window (520−420 ppm) for iron(III) C-methylated N-confused porphyrin which remains in contrast with relatively small values of iron(II) C-methylated derivatives (50−80 ppm). The results reported here demonstrate that dioxygen reacts cleanly with **2** carbaporphyrin to form the corresponding five-coordinate intermediate-spin iron(III) complexes **5** but contrary to 2-aza-21-carbaporphyrin its N-methylated derivative could not acquire the oxo functionality. Similarly, the C−*Me* group, positioned near the center of the carbaporphyrin, presents a serious steric barrier that plays an essential role in governing iron C-methylated N-confused porphyrin reactivity. For instance, the iron(II) dimethylated N-confused porphyrins undergoes solely one-electron oxidation. Further investigations of the iron carbaporphyrinoid complexes are expected to afford a unique insight into the reactivity of a metal−carbon bond as specifically tuned carbaporphyrins can be expected to have influence on the feasible pathways of the oxygenation processes.

Experimental Section

Materials. N-confused porphyrin (CTPP*H*)H$_2$ and its methylated derivatives (*Me*CTPP*H*)H, (*H*CTPP*Me*)H, and (*Me*CTPP*Me*)H have been obtained by already described methods.[29−33,44] Chloroform-*d* used in ^{1}H NMR was deacidified by passing down a basic alumina column. Dichloromethane-d_2 and chloroform-*d* were degassed by the freezing−pumping−thawing method and stored in a dry glovebox.

Iron(II) Insertion into Methylated N-Confused Porphyrins. Insertion of iron(II) was carried out under purified nitrogen in a glovebox. Iron(II) bromide was prepared by stirring of 0.10 g (0.5 mmol, 5 equiv) of commercially available iron(II) bromide and excess (ca. 1 g) iron powder in THF (distilled from sodium under N$_2$) under N$_2$ until the solution became colorless. The iron powder was removed. Subsequently, the solution of the appropriate methylated N-confused porphyrin (ca. 1 equiv, 60 mg in THF/acetonitile) and aliquot of 20 μL of collidine was added. The solution was stirred at 60 °C for 3 h. The insertion was quantitative as checked by ^{1}H NMR. The volume was reduced to 30%. After 12 h the solid residue was filtered out, washed with acetonitrile, and vacuum-dried. The iron(II) complexes were eventually crystallized from the dichloromethane/hexane mixture. MS (ESI, *m*/*z*): **2**, 763.2 (763.1 calcd for [$C_{45}H_{31}BrFeN_4 + H^+$]); **3**, 763.5 (763.1 calcd for [$C_{45}H_{31}BrFeN_4 + H^+$]); **4**, 777.4 (777.1 calcd for [$C_{46}H_{33}BrFeN_4 + H^+$]).

NMR Studies. The solution of iron(II) inverted porphyrin in a deuterated solvent was been prepared under purified nitrogen in a glovebox. The solution was directly placed into an ^{1}H NMR tube and sealed with a septum cap. In titration experiments, a solution of the oxidizing reagent in the deuterated, deoxygenated solvent was added to the sample through a microsyringe. A stepwise addition of dioxygen was carried out by titration with the deuterated solvent saturated with dioxygen. The progress of the reaction was followed by ^{1}H NMR.

Instrumentation. ^{1}H NMR (300 and 500 MHz) spectra were measured on Bruker AMX 300 and Bruker Avance 500 spectrometers. The peaks were referenced against the residual resonances of the deuterated solvents.

Acknowledgment. This work was supported by the Ministry of Scientific Research and Information Technology of Poland under Grant 3 T09A 162 28.

Supporting Information Available: VT NMR data for **2**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

IC061092H

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