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Novel routes for the modification of iron porphyrins

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Abstract

The effects of unconventional modifications of iron tetraarylporphyrins on their electronic structure and chemical properties were examined. The alterations included the β(*meso*)-substitution or an oxygen atom insertion into an iron–nitrogen bond. The profound transformation of porphyrin to 2-pyridiniumylporphyrin, isoporphyrin or porphodimethene occurred in reactions involving iron porphyrin in highly-oxidized states and pyridine. Addition of 2,4,6-collidine generated iron porphyrin N-oxides. The 2-hydroxy substituted tetraphenylpor-

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phyrin (a hybrid-type ligand) coordinates using a tetranitrogen macrocyclic center and an ionized hydroxy group of the periphery to form the cyclic trimer [(2-O–TPP)Fe(III)]$_3$. The seven pyrrole protons of (2-X-TPP)Fe(III)Cl and [(2-X–TPP)Fe(III)(CN)$_2$] provided the direct probe of the spin density distribution around the porphyrin macrocycle as determined by ^{1}H-NMR. Studies on the controlled modification of the tetraarylporphyrin periphery also included a symmetrical modification of a single pyrrole ring to obtain iron(III) quinoxalinoporphyrin characterized by the less common $(d_{xz}d_{yz})^4(d_{xy})^1$ low-spin ground electronic state of the bis-cyanide derivative [(QTPP)Fe(III)(CN)$_2$]$^-$.

Keywords: Iron porphyrins; Cation radicals; NMR

1. Introduction

Research interest in the function, stabilization and electronic and molecular structure of highly oxidized metalloporphyrins including iron porphyrin π-cation radicals results from the crucial importance of high-valent intermediates in enzymatic cycles of hemoproteins (peroxidases, catalases, cytochrome P-450, cytochrome *c* oxidase) and in catalytic reactions of iron porphyrins [1–6]. Reversible one- or two-electron oxidations of iron(III) porphyrin to form ferryl porphyrin or ferryl porphyrin π-cation radical, respectively, were established in the course of these studies. Considerable effort has been directed to elaborate the mechanism of the reactions where the highly oxidized porphyrins are generated in the activation and transfer of oxygen, particularly in catalytic epoxidation/hydroxylation processes [2,4–8]. The same heme/dioxygen combination is used in nature to destroy unwanted hemes via iron oxophlorin intermediates [9].

The catalytic reactions involving metalloporphyrins are frequently accompanied by catalyst degradation. Introduction of perhalogenated porphyrins improved the stability of catalysts [5,6]. Chemically, in our understanding, the degradation process should be considered as a stepwise route which engages several metalloporphyrin-like intermediates. Consequently the comprehension of the catalytic system reactivity should include deeper insight into the structure of the transformed catalytic centers assuming that they do preserve the basic features of metalloporphyrin. Therefore, the intermediate species may generate their own catalytic path. In general, the reactivity of highly oxidized iron porphyrins, including iron(III) porphyrin π-cation radical complexes has received relatively little study. The present brief review presents the account of investigations aimed in such a direction. The detection of modified metalloporphyrins requires an analysis of the paramagnetically shifted ^{1}H-NMR and ^{2}H-NMR spectra in selected spin/ligation states for independently synthesized spectroscopic models since the paramagnetically shifted porphyrin resonances provide a convenient and sensitive marker which allows the various species to be easily detected and identified [10].

2. Highly oxidized metalloporphyrins—reactivity with involvement of a porphyrin fragment

Taking into consideration the reactivity of highly oxidized metalloporphyrins at their periphery, illustrative examples of the biochemical and catalytic aspects of the topic of interest have been chosen for the presentation. The destruction of hemoglobin and myoglobin by arylhydrazines in the presence of dioxygen leads to the precipitation of Heinz bodies and the formation of green pigments, identified as *N*-phenylhemes [11–13]. The formation of *N*-substituted porphyrins via iron(III) and iron(IV) intermediates has been demonstrated to be involved in the deactivation of hemoproteins [14–17]. Additionally alkylhydrazines produce *meso*-alkylation products when reacted with myoglobin [18]. Synthetic iron *meso*-tetraphenylporphyrins which are able to catalyze the oxidation of olefins with non-physiological oxidants (iodosylarenes or hypochlorite) also undergo *N*-alkylation during the catalytic cycle [19]. Oxidative heme catabolism, either by heme oxygenase or by the coupled oxidation procedure results in the removal of the methine group from the iron porphyrin with the eventual release of carbon monoxide, iron and biliverdin [9]. Three molecules of dioxygen are involved in the reaction and the process involves initial *meso* hydroxylation of the heme. Highly oxidized forms of myoglobin react with thiols to form sulfmyoglobin with an insertion of sulfur at the β-pyrrole position(s) [20]. It was demonstrated that highly oxidized iron porphyrins react at the *meso* position and this is related to topology of the hemoprotein crevice [18,21–23]. The reaction of horse myoglobin with H_2O_2 results in covalent binding of the heme prosthetic group to the protein via tyrosine-103 [21,22]. The *meso* addition of radicals to the prosthetic group of horseradish peroxidase was also established [23]. It was also suggested that highly oxidized iron porphyrin complexes generate iron porphyrin π-cation radicals or protein radicals even if the oxidizing equivalent is initially present as Fe(IV) or Fe(IV)O (ferryl) [24,25]. Thus, understanding the elementary degradation steps for both biochemical and synthetic systems requires better knowledge of the iron porphyrin π-cation radical reactivity. Initially, two distinct routes of reactivity of the diperchlorate iron(III) tetraphenylporphyrin π-cation radical complex were established: (a) one-electron reduction, or (b) intramolecular electron transfer due to axial coordination [26]. Outer-sphere, one-electron transfer from bromide, iodide or 1,8-bis(dimethylamino)naphthalene resulted in the formation of iron(III) porphyrin complexes. In the presence of bases with a high oxidation potential (such as pyridine), $[(TPP)Fe(III)–O–Fe(III)(TPP^{\bullet})]^{+}$ was formed [26]. Imidazole (Im) ligands converted the high-spin iron(III) porphyrin π-cation radical to a low-spin iron(III) porphyrin π-cation radical [27]. The titration of ferryl porphyrin π-cation radical with Im yielded the corresponding $[(Im)(P^{\bullet})Fe(IV)O]^{+}$ species, although excess of nitrogen base resulted in reduction [28]. Coordination of methoxide to the iron(III) porphyrin π-cation radical caused the conversion to the iron(IV) porphyrin [29]. Iron(III) tetramesitylporphyrin π-cation radical $(TMP^{\bullet})Fe(III)(ClO_4)_2$ was used as a convenient oxidizing agent to generate $[(TMP^{\bullet})Fe(IV)O]^{+}$ from (TMP)Fe(IV)O [30].

There has been a considerable body of work done on porphyrin radical complexes of diamagnetic metal ions [31–35]. Typical reactions with a wide variety of nucleophiles, including pyridine, produced metalloporphyrins and β- or *meso*-substituted metalloporphyrins. The formation of *meso*-substituted isoporphyrins and bilitrienes was also observed for selected nucleophiles. The reactivity of the iron(III) porphyrin π-cation radicals has received little study. A contribution of iron tetraphenylporphyrin π-cation radical was considered in the generation of iron(III) 2-nitrotetraphenylporphyrin in the reaction of (TPP)Fe(III)Cl with NO_2 [36]. Reaction of (OEP)Fe(III)Cl with NO_2 produced (5-NO_2–OEP)Fe(III)Cl [37]. Two equivalents of hydroperoxide oxidize iron(III) tetra-(4-methoxyphenyl)porphyrin to the corresponding isoporphyrin [38].

3. Reactions of the iron(III) tetraphenylporphyrin π-cation radical with selected nucleophiles

Addition of triphenylphosphine, nitrite anion or pyridine to iron(III) tetraphenylporphyrin π-cation radical (TPP$^{\bullet}$)Fe(III)$(ClO_4)_2$ resulted in isolation of β-substituted derivatives, (2-PPh_3–TPP)Fe(III)Cl_2, (2-NO_2–TPP)Fe(III)Cl and (2-py–TPP)Fe(III)Cl_2, as the only stable, ring-modified products in the reaction mixture [39,40]. The X-ray structure of (2-PPh_3–TPP)Fe(III)Cl_2 (Fig. 1) presents a rare case of a six-coordinate high-spin iron(III) porphyrin complex [39].

Since the ^{1}H-NMR (^{2}H-NMR) spectra of iron porphyrins offer a sensitive technique for distinguishing between the various spin oxidation states of iron porphyrins [10], this spectroscopy has been used as the principal method for

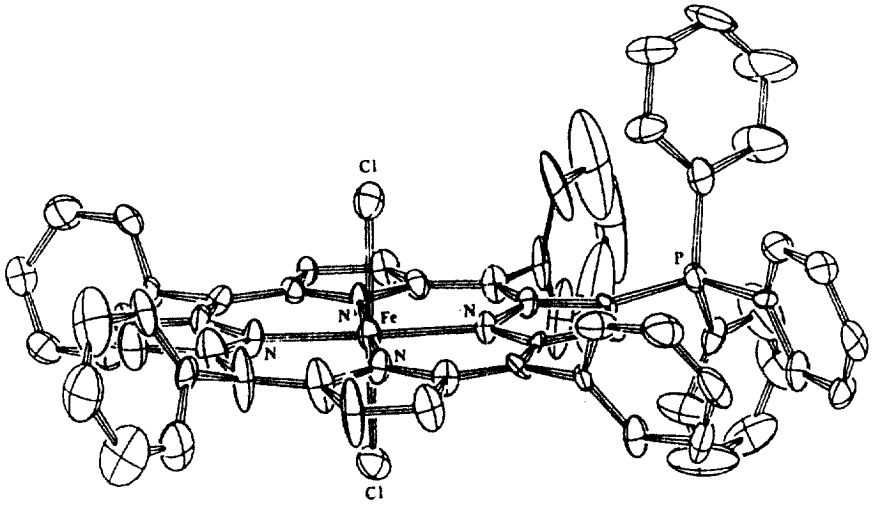
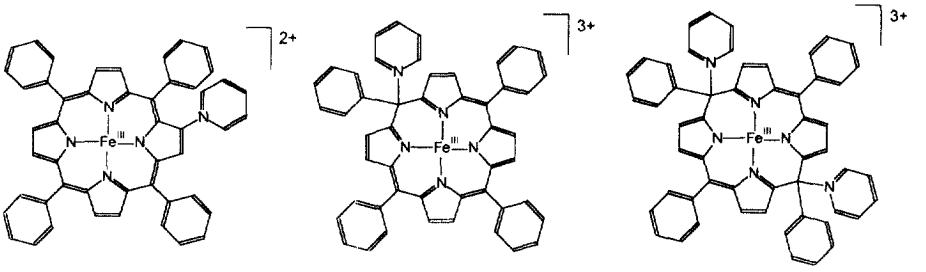


Fig. 1. Perspective view of (2-PPh_3-TPP)Fe(III)Cl_2 showing 50% thermal contours. Reprinted with permission from Ref. [39]. Copyright 1991 American Chemical Society.



[(2-py-TPP)Fe^{III}]$^{2+}$ [(5-py-TPP)Fe^{III}]$^{3+}$ [(5,15-di-py-TPP)Fe^{III}]$^{3+}$

Scheme 1.

following the reaction of the iron porphyrin π-cation radical with selected nucleophiles or proton scavengers. In anticipation of the thermal instability of the fundamental reaction intermediates the respective measurements were routinely carried out in dichloromethane-d_2 solutions at low temperature in order to trap conceivable transient forms.

Iron(III) tetraphenylporphyrin π-cation radical complexes, [(TPP$^{\bullet}$)Fe(III)Cl]-[$SbCl_6$] and (TPP$^{\bullet}$)Fe(III)(ClO_4)$_2$, reacted with pyridine at 193 K [40]. Spectroscopic evidence was obtained for the substitution of the porphyrin ring with pyridine with formation of thermally stable 2-pyridiniumyltetraphenylporphyrin, and unstable 5-pyridiniumyltetraphenylisoporphyrin, and 5,15-dipyridiniumyltetraphenylporphodimethene, complexes of iron (Scheme 1).

meso-Substituted forms [(5-py–TPP)Fe(III)]$^{3+}$ and [(5,15-di-py-TPP)Fe(III)]$^{3+}$ were directly observed over the temperature range 193–233 K. The characteristic patterns of paramagnetically shifted pyrrole resonances (i.e. seven for β-substituted form, four for isoporphyrin, two for porphodimethene iron complexes), correlate with the symmetry of the species and provide a definitive indication of porphyrin structural modifications. The pyridine substituted iron porphyrins are simultaneously generated in different oxidation/electronic/spin states. The overall stoichiometry is shown in the following equations:

$$2[(TPP^{\bullet})Fe(III)]^{2+} + 2py \rightleftharpoons [(2\text{-py–TPP})Fe(III)]^{2+} + [(TPP)Fe(III)]^{+} + pyH^{+}$$

$$[(TPP^{\bullet})Fe(III)]^{2+} + py \rightleftharpoons [(5\text{-py–TPP})Fe(III)]^{3+} + [(TPP)Fe(III)]^{+}$$

$$[(5\text{-py–TPP})Fe(III)]^{3+} + py \rightleftharpoons [(5,15\text{-di-py–TPP})Fe(III)]^{3+}$$

Three different mechanistic pathways should be taken into account for reactions of metalloporphyrin π-cation radical with nucleophiles [31–35,40,41]:

1. Iron porphyrin π-cation radical is attacked by a nucleophile at the *meso* or β-position to give a σ-adduct that is still a radical. Subsequent one-electron oxidation and/or proton dissociation gives the expected β-(*meso*)-substitution product.

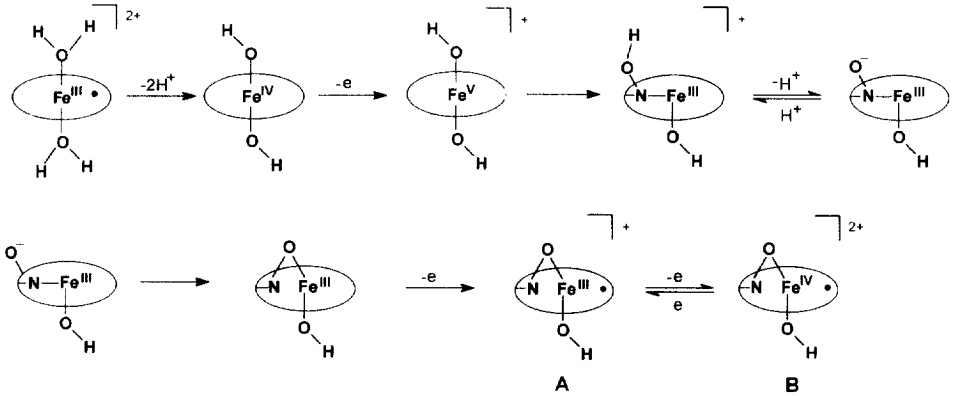
2. The reaction proceeds via a dication formed by disproportionation of the π-cation radical. The dication reacts rapidly with nucleophiles.
3. Iron porphyrin π-cation radical couples with a radical that was formed by one electron oxidation of the nucleophile.

Route 3, although feasible for the β-NO_2 or β-PPh_3 substitution, i.e. in the case of easily oxidizable nucleophiles [39] should be dismissed in the case of pyridine. The oxidation of pyridine to give the corresponding radical would require a higher oxidation potential than that achievable by iron(III) tetraphenylporphyrin π-cation radicals. At the present stage, none of the plausible σ-intermediates in the β-substitution mechanisms could be directly identified by means of the methodology applied. The formation of the *meso*-substituted species $[(5\text{-py–TPP})Fe(III)]^{3+}$ and $[(5,15\text{-di-py–TPP})Fe(III)]^{3+}$ is of special interest. Formally, they are oxidized by two electrons with respect to iron(III) porphyrins. Thus, they represent a new form of highly oxidized, positively charged iron porphyrin related species.

4. Disproportionation of iron(III) porphyrin π-cation radicals

The replacement of pyridine by the sterically hindered derivatives (2,4,6-collidine, 2,3,6-collidine, 2-picoline, 2,6-di-*tert*-butylpyridine) forces alternative transformation routes [42]. Iron(III) tetraphenylporphyrin π-cation radical $(TPP^{\bullet})Fe(III)(ClO_4)_2$, iron(III) tetra-*p*-tolylporphyrin π-cation radical $(TTP^{\bullet})Fe(III)(ClO_4)_2$ and iron(III) tetramesitylporphyrin π-cation radical $(TMP^{\bullet})Fe(III)(ClO_4)_2$ undergo hydration processes. The hydrated species are essential in the generation of highly oxidized forms via disproportionation, preceded by acid/base equilibria of coordinated water. Here the 2,6-disubstituted pyridines act as efficient proton scavengers.

The low-temperature ^{1}H-NMR investigations revealed the complex reaction mechanism (Scheme 2). Two novel porphyrin *N*-oxide complexes, i.e. iron(III)



Scheme 2.

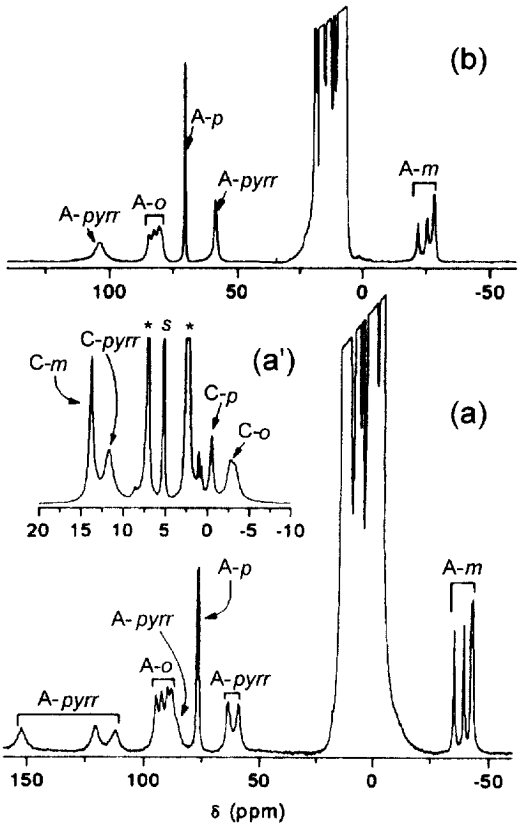


Fig. 2. The 300 MHz ^{1}H-NMR spectra of a dichloromethane-d_2 solution of (TPP$^{\bullet}$)Fe(III)$(ClO_4)_2$ after addition of two equivalents of 2,4,6-collidine (a) at 202 K, (b) at 232 K. Inset in Trace (a') presents an expansion of the +20 to −10 ppm region (202 K). Compounds are labeled as in the text: **A**, [(TPP$^{\bullet}$–N–O)Fe(III)(OH)]$^+$, **C**, [(TPP)Fe(III)OFe(III)(TPP$^{\bullet}$)]$^+$; subscripts refer to assignments: pyrr, porphyrin pyrrole protons; o, m, p, *ortho*, *meta*, *para* phenyl protons; s, solvent; *, 2,4,6-collidine. Reprinted with permission from Ref. [42]. Copyright 1996 American Chemical Society.

porphyrin *N*-oxide π-cation radical, [(TPP$^{\bullet}$–N–O)Fe(III)(OH)]$^+$ or [(TTP$^{\bullet}$–N–O)Fe(III)(OH)]$^+$ (Scheme 2, form **A**) and iron(IV) porphyrin *N*-oxide radical ([(TTP$^{\bullet}$–N–O)Fe(IV)(OH)]$^{2+}$, **B**) have been identified. Simultaneously [(TPP)Fe(III)OFe(III)(TPP$^{\bullet}$)]$^+$ or [(TTP)Fe(III)OFe(III)(TTP$^{\bullet}$)]$^+$ (**C**) were detected as sole thermally stable products.

The ^{1}H-NMR results indicate that the D_{4h} symmetry of the parent iron(III) π-cation radical is drastically reduced upon disproportionation in the presence of proton scavengers. Both species are very unstable and exist in the narrow 176–232 K temperature range. The remarkable large hyperfine shifts for *meso*-phenyls ([(TPP$^{\bullet}$–N–O)Fe(III)(OH)]$^+$): *ortho* 94.8, 92.4, 89.9, 88.1 ppm; *meta* −35.0, −39.2, −42.4, −42.8 ppm; *para* 77.1, 76.7 ppm, and *meso*-*p*-tolyls ([(TTP$^{\bullet}$–N–O)Fe(III)(OH)]$^+$): *ortho* 98.0, 94.8, 92.9, 91.7 ppm; *meta* −34.8, −38.7, −42.5,

−42.3 ppm; *p*-CH_3 −86.3, −88.0 ppm) confirm the presence of *N*-substituted iron porphyrin radicals (Fig. 2).

Characteristic ^{1}H-NMR shifts of $[(TTP^{\bullet}-N-O)Fe(III)(OH)]^+$ include six pyrrole resonances at 152.5, 120.7, 112.8, 85.4, 63.9, 59.4 ppm at 202 K, i.e. in the positions corresponding to high-spin iron(III) porphyrin cation radicals. On warming to 222 K the pyrrole resonances broaden and then coalesce pairwise. Such a dynamic behavior has been accounted for by a rearrangement mechanism which involves an inversion of the porphyrin puckering. The pattern of *p*-tolyl resonances revealed the π-cation radical electronic structure of $[(TTP^{\bullet}-N-O)Fe(IV)(OH)]^{2+}$. The *p*-tolyl resonances are divided into two distinct sets with opposite direction of the isotropic shift for the same ring positions. Additionally, the pyrrole resonances also demonstrated downfield and upfield shifts. Both new intermediates (**A** and **B**) react with triphenylphosphine to produce triphenylphosphine oxide and high-spin iron (III) porphyrins.

Contrary to sterically unprotected iron porphyrins, addition of 2,4,6-collidine to $(TMP^{\bullet})Fe(III)(ClO_4)_2$ does not generate respective analogs of $[(TTP^{\bullet}-N-O)Fe(III)(OH)]^+$ and $[(TTP^{\bullet}-N-O)Fe(IV)(OH)]^{2+}$. Instead the formation of a variety of ferryl(IV) porphyrin π-cation radicals $[X(TMP^{\bullet})Fe(IV)O]^+$ was unambiguously detected. The novel route to generate this well known highly oxidized species [8,25] was accounted for by a mechanism involving acid–base equilibria and a disproportionation step:

$$[(X)(TMP^{\bullet})Fe(III)(H_2O)]^{2+} + coll \rightarrow [(X)(TMP^{\bullet})Fe(III)(OH)]^+ + collH^+$$

$$[(X)(TMP^{\bullet})Fe(III)(OH)]^+ + coll \rightarrow \{(X)(TMP^{\bullet})Fe(III)(O^-)\} + collH^+$$

$$\{(X)(TMP^{\bullet})Fe(III)(O^-)\} \rightarrow (TMP)Fe(IV)O + X$$

$$\mathbf{(TMP)Fe(IV)O} + [(X)(Y)(TMP^{\bullet})Fe(III)]^{2+}$$

$$\rightarrow \mathbf{[(Y)(TMP^{\bullet})Fe(IV)O]}^+ + [(TMP)Fe(III)X]^+$$

(X, Y, the neutral ligands generated in the system; if X or Y are monoanions, the overall charge of corresponding forms should be appropriately lowered).

5. Reaction of iron(III) porphyrin π-cation radical with the phenyl Grignard reagent

One-electron oxidation of σ-phenyl iron(III) porphyrin complexes produced corresponding σ-phenyl iron(IV) derivatives [17]. The alternative approach, namely a generation of the iron(III) porphyrin π-cation radical via one-electron oxidation of the iron(III) porphyrin, followed by its reaction with the phenyl (*p*-tolyl) Grignard reagent was followed by ^{1}H-NMR [43]. This process yields the mixture of σ-phenyl iron(IV) tetraphenylporphyrin, $[(TPP)Fe(IV)(Ph)]^+$, and σ-phenyl iron(III) tetraphenylporphyrin, (TPP)Fe(III)Ph. Thus the new procedure to generate σ-aryl iron(IV) porphyrin species, starting from the iron(III) porphyrin π-cation radical, has been established.

$$[(TPP^{\bullet})Fe(III)]^{2+} + Ph^{-} \rightarrow \{[(TPP^{\bullet})Fe(III)Ph]^{+}\} \rightarrow [(TPP)Fe(IV)Ph]^{+}$$

A concurrent nucleophilic addition to the tetraphenylporphyrin macrocycle, accompanied by the σ-phenyl iron(III) axial coordination, was detected as well. A diagnostic ^{1}H-NMR pattern of the low-spin iron(III) porphyrin ring modified species reflects its C_s symmetry and includes four upfield shifted pyrrole resonances (2.31; −10.40; −20.39; −20.87 ppm, 202 K) and a set of σ-phenyl resonances (*o*-H, −188.4; *p*-H, −102.5; *p*-CH_3 for σ-*p*-tolyl, 162.3 ppm). The formation of the low-spin σ-phenyliron(III) isoporphyrin or low-spin σ-phenyl N-arylporphyrin has been considered.

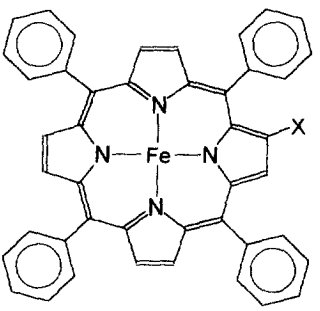
$$2[(TPP^{\bullet})Fe(III)]^{2+} + 2Ph^{-} \rightarrow [(\textit{meso}\text{-}Ph\text{-}TPP)Fe(III)Ph]^{+} + [(TPP)Fe(III)]^{+}$$

The *meso* substitution can be accounted for by the mechanism, which emphasizes the radical nature of the reaction substrate and involves the formation of σ-transient forms.

6. ^{1}H-NMR investigation of β-substituted high-spin and low-spin iron(III) tetraphenylporphyrins

The β-substituted iron(III) tetraphenylporphyrins have been unambiguously identified as stable products in the reaction of iron porphyrin π-cation radicals with selected nucleophiles [39,40]. Consequently, some interest has been developed in spectroscopic and reactivity aspects of β-substituted iron(III) tetrarylporphyrins (Scheme 3) in general.

The ^{1}H-NMR spectra of iron(III) complexes of β-substituted tetraphenylporphyrins (2-X–TPP) were studied to elucidate the relationship between the electron donating/withdrawing properties of the 2-substituent and the ^{1}H-NMR spectral pattern [44]. The electronic nature of the substituent has been significantly varied and covered the −0.6 to +0.8 Hammett constant range. Both high-spin and low-spin complexes of the general formula (2-X–TPP)Fe(III)Cl and $[(2\text{-X–TPP})Fe(III)(CN)_2]^{-}$ have been investigated (X: py^{+}, NO_2, CN, CH_3, BzO (C_6H_5COO), H, D, Br, Cl, OCH_3, NH_2, NH_3^{+}, $NHCH_3$, OH, O^{-}). The ^{1}H-NMR



Scheme 3.

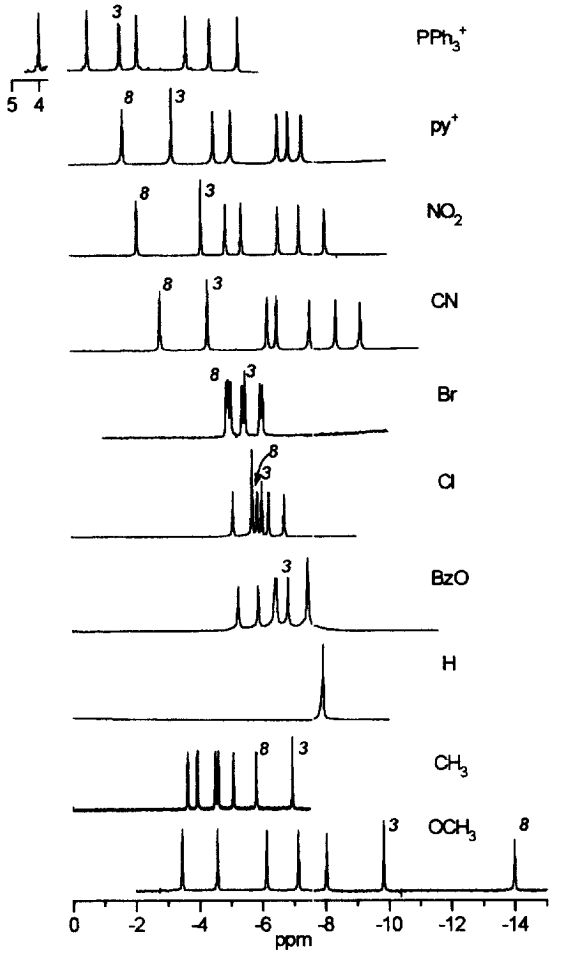


Fig. 3. 300 MHz ^{1}H-NMR spectra of the pyrrole region of a series of low spin $[(2\text{-X-TPP})Fe(III)(CN)_2]^-$ complexes in methanol-d_4 solutions at 293 K. X substituents marked on each trace. The most characteristic 3-H and 8-H pyrrole resonances labeled by *3* and *8*, respectively. Reprinted with permission from Ref. [44]. Copyright 1996 American Chemical Society.

resonances for low-spin dicyano complexes have been completely assigned by a combination of two-dimensional COSY and NOESY experiments. The pattern of seven pyrrole resonances (Fig. 3) reflects the asymmetry imposed by 2-substitution and has been used as a unique ^{1}H-NMR spectroscopic probe to map the spin density distribution.

The pyrrole isotropic shifts of $[(2\text{-X-TPP})Fe(III)(CN)_2]^-$ are dominated by the contact term. The dependence of isotropic shift of all low-spin pyrrole resonances and 3-H high-spin pyrrole resonance versus Hammett constants has been studied in order to quantify the substituent effect. The electronic effect is strongly localized at the β-substituted pyrrole: ^{1}H-NMR signal of 3-H proton shifts upfield when

Hammett constant of substituent X decreases. For low-spin complexes, the major change of the isotropic shift has also been noted for only one of two adjacent pyrrole rings i.e. at 7-H and 8-H positions. These neighboring protons, located on a single pyrrole ring, experienced opposite shift changes when electron withdrawing/donating properties were modified. Two other pyrrole rings for all investigated derivatives revealed considerably smaller, substituent related, isotropic shift changes.

A long-range secondary isotopic shift has been observed for [(2-D-TPP)Fe(III)$(CN)_2]^-$. The effect is consistent with a general spin density distribution mechanism due to β-substitution. For low-spin complexes, ^{13}C pyrrole resonances of carbons bearing a proton have been identified by means a $^1H-^{13}C$ HMQC experiment. The reversed order of ^{13}C pyrrole resonance patterns as compared to their ^1H-NMR counterparts has been determined e.g. the largest isotropic shift of 3-H has been accompanied by the smallest measured ^{13}C isotropic shift.

7. Iron(III) 2-hydroxy-5,10,15,20-tetraphenylporphyrin and its self-assembly

The importance of the β-substitution as the feasible route of the iron porphyrin degradation in oxidizing conditions was independently confirmed in the reaction of benzoyl peroxide with (TPP)Fe(III)Cl [45]. The benzoylation product, i.e. (2-benzoyloxy-TPP)Fe(III)Cl was directly detected by ^1H-NMR in the reaction mixture. In all probability, it is one of iron porphyrin degradation routes during catalytic processes. Consequently, the chemistry of 2-benzoyloxytetraphenylporphyrin and its hydrolysis product, 2-hydroxytetraphenylporphyrin needs to be viewed in the context of the fact that these particular porphyrins can likely be produced in the course of the iron tetraphenylporphyrin treatment with typical oxidizing reagents, triggering the new reaction pathways. 2-Hydroxytetraphenylporphyrin reveals an equilibrium between aromatic hydroxyl, enol, and keto tautomers [46]. Potentially it may demonstrate the unique features of a hybrid-type ligand in coordination using a tetranitrogen macrocyclic center and an ionized hydroxy group of the periphery. The self-assembly process of a monomeric metal ion(III) 2-hydroxy-5,10,15,20-tetraphenylporphyrin complex (2-OH-TPP)M(III)Cl (M(III): Fe(III), Mn(III), Ga(III)) affords the unusual cyclic trimeric complexes $[(2\text{-O-TPP})M(III)]_3$ [45,47–49]. The convenient synthetic procedure has been based on hydrolysis of (2-BzO-TPP)M(III)Cl according to the reaction:

$$3(2\text{-BzO-TPP})M(III)Cl + 6NaOH \rightarrow [(2\text{-O-TPP})M(III)]_3 + 3NaCl + 3BzONa + 3H_2O$$

The ^1H-NMR spectroscopic evidence indicated that these compounds have a head-to-tail cyclic trimeric structure with the pyrrolic–alkoxide groups forming bridges from one macrocycle to the metal ion in the adjacent macrocycle. The structure of $[(2\text{-O-TTP})Fe(III)]_3$ (Fig. 4) has been determined by X-ray crystallography [49]. The porphyrinic skeleton of $[(2\text{-O-TTP})Fe(III)]_3$ constitutes a common

pattern for homometallic and heterometallic trimeric iron(III), gallium(III) and manganese(III) complexes of 2-hydroxytetraarylporphyrin.

The presence of the three paramagnetic, weakly coupled high-spin iron(III) or manganese(III) centers in $[(2\text{-O-TPP})Fe(III)]_3$ or $[(2\text{-O-TPP}))Mn(III)]_3$ produces marked variation of positions and line widths for the pyrrole resonances (Fig. 5). The characteristic upfield positions of the 3-H pyrrole resonances (291 K) were determined and considered as the diagnostic feature for the iron(III) (-89.8, -94.7, -99.3 ppm) [45] and the manganese(III)–pyrrole alkoxide coordination (-111.5 ppm) [48].

The diamagnetic $[(2\text{-O-TPP})Ga(III)]_3$ trimer demonstrated unusual 3-H pyrrole resonance positions (1.82, 2.18, 2.82 ppm, 243 K) due to the ring current effect [47].

$[(2\text{-O-TPP})M(III)]_3$ complexes have been cleaved by protic acids (HX) to form monomeric five-coordinate species (2-OH–TPP)M(III)X. The stepwise cleavage mechanism was determined in the course of the titration with trifluoroacetic acid. The process involved the formation of linear dimeric intermediates [(2-OH–TPP)M(III)–(2-O–TPP)M(III)(TFA)] [45,47].

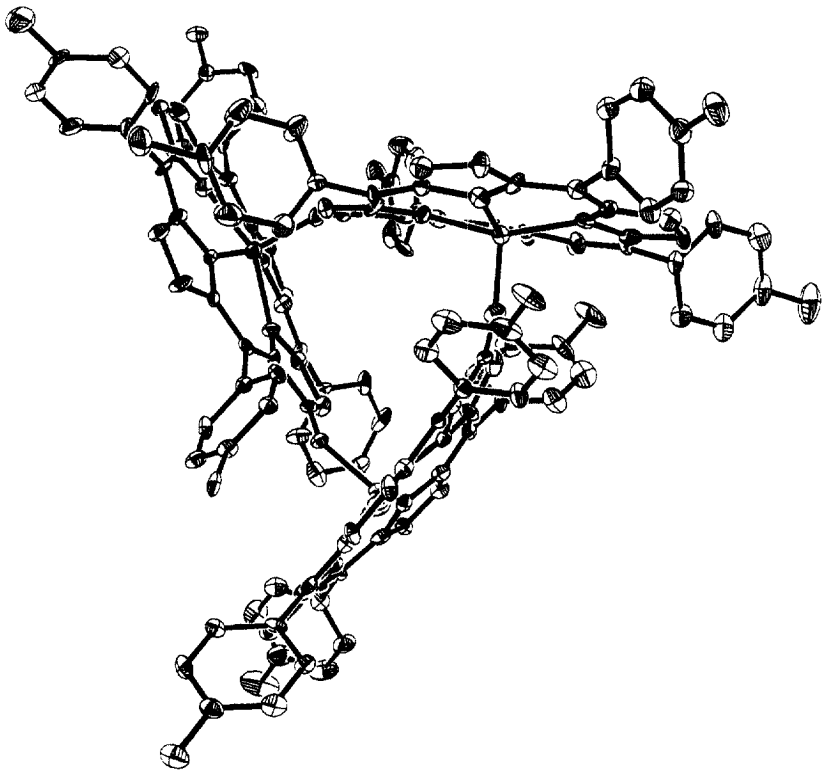


Fig. 4. Perspective view of $[(2\text{-O-TTP})Fe(III)]_3$ showing 20% thermal contours. Reprinted with permission from Ref. [49]. Copyright 1997 American Chemical Society.

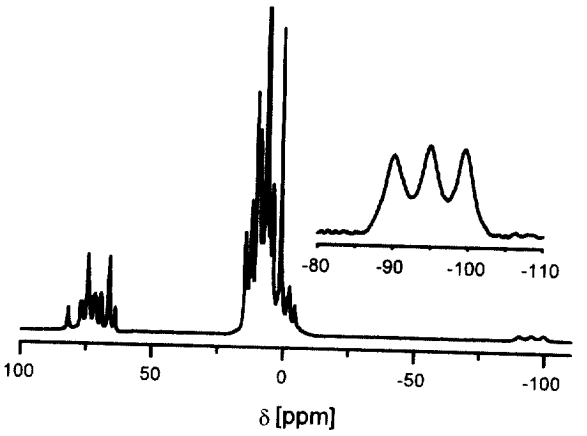


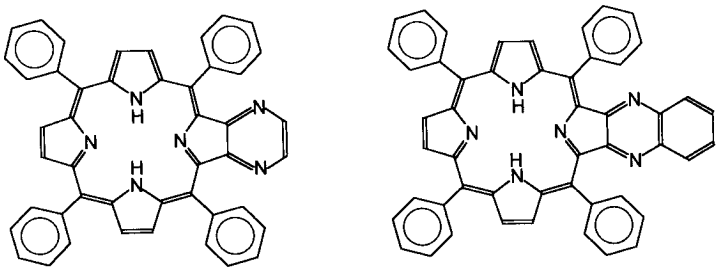
Fig. 5. ^{1}H-NMR spectrum of [(2-O–TPP)Fe(III)]$_3$ at 291 K. Inset shows 3-H pyrrole resonances. Reprinted with permission from Ref. [45]. Copyright 1995 American Chemical Society.

Oligomerization of a mixture of monomeric iron(III), manganese(III) and gallium(III) 2-hydroxy-5,10,15,20-tetraphenylporphyrins affords the series of heterometallic cyclic trimeric complexes of the general formula {[(2-O–TPP)Ga(III)]$_n$[(2-O–TPP)Fe(III)]$_{3-n}$}, {[(2-O–TPP)Ga(III)]$_n$[(2-O–TPP)Mn(III)]$_{3-n}$}, {[(2-O–TPP)Fe(III)]$_n$[(2-O–TPP)Mn(III)]$_{3-n}$} ($n = 0$–3). The ^{1}H-NMR and mass spectrometry investigation indicates that these compounds have a head-to-tail cyclic trimeric structure. The presence of the paramagnetic, weakly coupled paramagnetic centers produces marked variation of positions and line widths for the pyrrole resonances. The characteristic upfield positions of the 3-H pyrrole resonances (PFe–OPGa, −145 ppm; PGa–OPFe, 41–47 ppm; PMn–OPGa, −65 ppm; PGa–OPMn, −70 ppm; PFe–OPMn, −175 to −190 ppm; all at 293 K) were determined and considered as the diagnostic feature for the PM–OPM$_1$ motive [49].

8. ^{1}H-NMR investigation of high-spin and low-spin iron(III) quinoxalinotetraphenylporphyrin

2-Benzoyloxyporphyrin or 2-hydroxyporphyrin can be considered as an interesting starting point in the generation of the peripherally modified porphyrin [50]. For instance, benzoylation of tetraphenylporphyrin with hydrolysis to 2-hydroxytetraphenylporphyrin, followed by oxidation with SeO_2 yields 17,18-dioxo-5,10,15,20-tetraphenylchlorin. The condensation of dioxotetraphenylchlorin with 1,2-phenylenediamine or ethylenediamine gave quinoxalinotetraphenylporphyrin, QTPPH$_2$ and pyrazinotetraphenylporphyrin PTPPH$_2$ (Scheme 4) and, after metal insertion, their iron(III) complexes, (QTPP)Fe(III)Cl and (PTPP)Fe(III)Cl [51].

The ^{1}H-NMR spectra of (QTPP)Fe(III)X$_n$ and (PTPP)Fe(III)X$_n$ (X: halides, CN^-, nitrogen bases) indicated the impact of a symmetrical aromatic extension of



PTPPH$_2$ QTPPH$_2$

Scheme 4.

a single pyrrole ring on the electronic structure of corresponding high- and low-spin iron(III) porphyrin. Modification of the tetraphenylporphyrin by addition of the quinoxaline (pyrazine) fragment results in stabilization of the rare low-spin iron(III) $(d_{xz}d_{yz})^4(d_{xy})^1$ electronic ground state in the presence of axial cyanide ligands, which was also recently found for iron(III) tetraalkylporphyrins [52,53]. The more common $(d_{xy})^2(d_{xz}d_{yz})^3$ electronic ground state exists for the $[(QTPP)Fe(III)(4\text{-}NH_2\text{-}py)_2]^+$ and $[(QTPP)Fe(III)(1\text{-}MeIm)_2]^+$ species. Deviation from the Curie law observed for $[(QTPP)Fe(III)(CN)_2]^-$ suggests the Boltzmann equilibrium: $\{(d_{xz})^2(d_{yz})^2(d_{xy})^2(\Psi_{-1})^1 \leftrightarrow (d_{xz})^2(d_{yz})^2(d_{xy})^1(\Psi_{-1})^2\} \rightleftharpoons (d_{xz})^1(d_{yz})^2(d_{xy})^2(\Psi_{-1})^2 \rightleftharpoons (d_{xz})^2(d_{yz})^1(d_{xy})^2(\Psi_{-1})^2$, where Ψ_{-1} is related to the a_{2u} orbital of a regular porphyrin. For the very first time in the group of low-spin iron(III) tetraarylporphyrins, a sign reverse of the isotropic shift was established for pyrrole resonances in the course of the variable temperature studies. The structure of (QTPP)Fe(III)Cl was determined by X-ray crystallography. The (QTPP)Fe(III)Cl compound presents features of the high-spin five-coordinate iron(III) tetraphenylporphyrin. The quinoxalinotetraphenylporphyrin macrocycle assumes a saddle-like configuration.

9. Conclusion

High valent iron oxo species have been directly detected as active intermediates in several different oxidation reactions using iron porphyrin complexes as catalysts and oxygen atom donors (H_2O_2, PhIO, NaOCl, $KHSO_5$, O_3, dimethyldioxirane) [1–8,54]. The electronic structure of the active intermediates can be described as ferryl porphyrin π-cation radicals. The catalytic systems are frequently moderated by coordination of nitrogen bases. The investigation of reactivity of the iron porphyrin π-cation radicals in the presence of pyridine or its sterically hindered derivatives, investigated at low temperature in inert solvents, sheds some light on the role of π-cation radical nature on the stability of catalysts. The strategy used has made it possible to detect various intermediates formed using iron porphyrin π-cation radicals. In particular it has been shown that β- and *meso* substitution of

the otherwise innocent pyridine, may drastically modify the way in which oxidation equivalents are stored. The ability to generate highly oxidized ferryl porphyrin π-cation radicals from the hydrated form of (TMP•)Fe(III)$(ClO_4)_2$ in the presence of the proton scavenger is of particular significance. In our opinion the formation of stable β-substituted metalloporphyrins may be instrumental in the creation of parallel catalytic reaction pathways. The pronounced and unpredictable effects of β-substitution on the electronic and molecular structure of the respective iron porphyrins are worthwhile emphasizing. Thus, the stabilization of the rare low-spin $(d_{xz}d_{yz})^4(d_{xy})^1$ ground electronic state serves as an illustrative example of the influence of a single pyrrole ring modification on the properties of the iron center. The oligomerization of iron(III) 2-hydroxytetraphenylporphyrin provides access to the new class of the polymeric metalloporphyrin linked by the coordination bond.

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