Published in final edited form as:

J Inorg Biochem. 2009 February ; 103(2): 174–181. doi:10.1016/j.jinorgbio.2008.09.017.

Formation of Stable and Metastable Porphyrin- and Corrole-Iron (IV) Complexes and Isomerizations to Iron(III) Macrocycle Radical Cations

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Abstract

Oxidations of three porphyrin-iron(III) complexes (**1**) with ferric perchlorate, $\text{Fe}(\text{ClO}_4)_3$, in acetonitrile solutions at -40°C gave metastable porphyrin-iron(IV) diperchlorate complexes (**2**) that isomerized to known iron(III) diperchlorate porphyrin radical cations (**3**) when the solutions were warmed to room temperature. The 5,10,15,20-tetraphenylporphyrin (TPP), 5,10,15,20-tetramesitylporphyrin (TMP), and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) systems were studied by UV-visible spectroscopy. Low temperature NMR spectroscopy and effective magnetic moment measurements were possible with the TPP and TMP iron(IV) complexes. Reactions of two corrole systems, 5,10,15-*tris*(pentafluorophenyl)corrole (TPFC) and 5,15-*bis*(pentafluorophenyl)-10-*p*-methoxyphenylcorrole (BPFMC), also were studied. The corrole-iron(IV) chlorides reacted with silver salts to give corrole-iron(IV) complexes. The corrole-iron(IV) nitrate complexes were stable at room temperature. (TPFC)-iron(IV) tosylate, (TPFC)-iron(IV) chlorate, and (BPFMC)-iron(IV) chlorate were metastable and rearranged to their electronic isomers iron(III) corrole radical cations at room temperature. (TPFC)-iron(III) perchlorate corrole radical cation was the only product observed from reaction of the corrole-iron(IV) chloride with silver perchlorate. For the metastable iron(IV) species, the rates of isomerizations to the iron(III) macrocycle radical cation electronic isomers in dilute acetonitrile solutions were relatively insensitive to electron demands of the macrocyclic ligand but reflected the binding strength of the ligand to iron. Kinetic studies at varying temperatures and concentrations indicated that the mechanisms of the isomerization reactions are complex, involving mixed order reactivity.

Keywords

high-valent; iron; porphyrin; corrole; oxidation; isomerization; valence tautomer

Introduction

Reactions of high-valent iron complexes have attracted considerable interest because iron-oxo intermediates are formed in catalytic oxidations in the laboratory and in nature [1–4]. In a typical catalytic sequence, an iron(III) species is oxidized to an iron-oxo transient with a formal oxidation state of +5 on iron by a peroxy- or oxo-containing sacrificial oxidant, and the high-valent iron-oxo species then oxidizes a substrate in a two-electron, oxo-transfer process to return the iron(III) complex [5–7]. Synthetic porphyrin-iron complexes and related corrole-iron complexes mimic heme-containing peroxidase and cytochrome P450 enzymes, and high valent iron-oxo species with both types of macrocycles have been known for years [8,9]. The

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aromatic macrocycle ligands provide unique energy manifolds for high-valent iron atoms in comparison to saturated multidentate ligands because the macrocycle can be oxidized to a radical cation permitting, for example, a formal iron(V)-oxo derivative to exist in a more stable electronic configuration as a iron(IV)-oxo macrocycle radical cation [10,11].

In principle, a macrocycle-iron⁺ⁿ species and its analogous iron⁺⁽ⁿ⁻¹⁾-macrocycle radical cation can be resonance forms of one another. When an energy barrier exists for electron transfer between the macrocycle and the iron atom, the two species will be isomers of one another, specifically electronic isomers (electromers) that are also known as valence tautomers [12]. The barriers that isolate the isomers from one another kinetically can be reasonably large due to, for example, considerable differences in bond lengths and relative atom positions. Thus, it is possible that the higher energy electromer or tautomer can react by an alternative pathway faster than it decays to the thermodynamically favored species by internal electron transfer relaxation. This reaction pathway might be important in some catalytic oxidations where, for example, a transient porphyrin-iron(V)-oxo species formed by reaction of a porphyrin-iron(III) complex with a sacrificial oxidant could be a reactive oxidant in catalytic oxidations even if not detected, whereas the better-known iron(IV)-oxo porphyrin radical cation might be a sluggish oxidant formed as a side-product of the major oxidation pathway [6,7,13].

True iron(V)-oxo species are rare. Que and co-workers reported formation of a tridentate ligand iron(V)-oxo complex [14], and evidence for another such species has been reported [15]. In the case of aromatic macrocyclic ligands, no iron(V)-oxo species has been fully characterized, but highly reactive iron-oxo transients produced in photochemical ligand cleavage reactions with both porphyrin [16] and corrole [9] macrocycles were tentatively assigned as iron(V)-oxo species. Computational studies [10,11] and thermodynamic cycles [17] suggest that macrocycle-iron(V)-oxo complexes should be energetically accessible, *i.e.* they should lie within several kcal/mol from their iron(IV)-oxo macrocycle radical cation electromers, but the iron(IV)-oxo macrocyclic radical cations are predicted to be the energetically favored species in most cases. Interestingly, corrolazine-iron(V)-oxo species [18] are predicted to be more stable than their iron(IV) macrocycle radical cation isomers [19].

For high-valent iron-macrocycle complexes with a formal +4 oxidation state of the metal, the energies of the iron(IV) complexes with “neutral” macrocycles and their iron(III) macrocycle radical cation electronic isomers apparently are closely matched. Understanding the position of oxidation in porphyrin-iron(III) complexes was an important objective in the chemistry of high-valent iron species [12,20], and studies of the position of oxidation in corrole-iron(III) complexes are contemporary [21]. The thermodynamically favored species in this class of complexes can switch from the iron(IV) “neutral” macrocycle to the iron(III) macrocycle radical cation as a function of the axial ligand binding strength [22,23], the pH of an aqueous solution [20], and the substitution on the macrocycle [12]. Complexes with formal +4 oxidation on iron are more stable than the more highly oxidized formal +5 iron-oxo complexes, and they provide an opportunity to study the mechanisms and barriers for interconversion of electronic isomers [16,24]. In this work, we report the production and studies of stable iron(IV) “neutral” macrocycle (porphyrin and corrole) complexes and metastable iron(IV) complexes that convert to their iron(III) macrocycle radical cation isomers. Similar behavior for porphyrin-manganese (IV) species and their manganese(III) porphyrin radical cations was reported previously [25].

Materials and Methods

Materials

HPLC grade acetonitrile (99.9%) was obtained from Sigma-Aldrich. Chloroform and methylene chloride were obtained from Fisher Scientific. All solvents were distilled prior to

use. All chemical reagents were purchased from Sigma-Aldrich Co. Analyses were performed by Atlantic Microlab, Inc.

Porphyrin complexes

The macrocycles for the porphyrin (Por) complexes were 5,10,15,20-tetraphenylporphyrin (TPP), 5,10,15,20-tetramesitylporphyrin (TMP), and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP). (TPP)Fe^{III}(Cl) and (OEP)Fe^{III}(Cl) were purchased from Sigma-Aldrich Co. The TMPH₂ free ligand and the (TMP)Fe^{III}Cl complex were prepared by reported methods [26, 27]. (TPP)Fe^{III}(ClO₄) (**1a**), (TMP)Fe^{III}(ClO₄) (**1b**), and (OEP)Fe^{III}(ClO₄) were prepared by reported methods [23,26–28]. Authentic samples of (TPP)⁺Fe^{III}(ClO₄)₂ (**3a**), (TMP)⁺Fe^{III}(ClO₄)₂ (**3b**), and (OEP)⁺Fe^{III}(ClO₄)₂ (**3c**) were prepared by reported methods [23,29,30].

Porphyrin-iron(IV) diperchlorate complexes (2)

In a typical reaction, solutions of **1a** (20 μM in CH₃CN) and Fe(ClO₄)₃ (0.5 mM in CH₃CN) were loaded into two gas-tight syringes. The solutions (200 μL each) were simultaneously injected into a stopped-flow optical cell in the UV-visible spectrometer. The data was analyzed with Applied Photophysics software. Decay or growth traces measured in Q-band regions were well fit to single exponential functions.

Corrole complexes

The macrocycles for the corrole (Cor) complexes were 5,10,15-*tris*(pentafluorophenyl)corrole (TPFC) and 5,15-*bis*(pentafluorophenyl)-10-*p*-methoxyphenylcorrole (BPFMC). The free ligands (TPFC)H₃ and (BPFMC)H₃ were prepared according to reported methods [31,32]. (TPFC)Fe^{III}(Et₂O)₂ and (TPFC)Fe^{IV}Cl (**4a**) were prepared by the reported method [21]. The corrole (Cor) species studied in this work are shown in Chart 2. The corrole systems were 5,10,15-*tris*(pentafluorophenyl)corrole (TPFC) and 5,15-*bis*(pentafluorophenyl)-10-*p*-methoxyphenylcorrole (BPFMC).

(BPFMC)Fe^{IV}Cl (**6a**)

The procedure described for insertion of iron into the (TPFC) ligand [21] was used to prepare (BPFMC)Fe^{III}(OEt₂)₂. Thus, 80 mg (0.1 mmol) of the free ligand and 0.25 g (2 mmol) of iron (II) chloride in DMF was heated at reflux under nitrogen for 30 min. The process was monitored by TLC (silica gel, hexanes/methylene chloride, 2:1). Evaporation of solvent followed by column chromatography (silica gel, ether) resulted in isolation of (BPFMC)Fe^{III}(OEt₂)₂ (75 mg, 0.08 mmol, 80%). UV-visible (CH₃CN): λ_{max}, nm (log ε), 406 (4.75), 550 (1.58). ¹H NMR (CDCl₃): δ 15.67 (s, 4H), 7.15–7.92 (m, 4H), 4.07 (s, 3H), –59.13 (s, 1H), –64.91 (s, 1H), –124.50 (br s, 2H). LRMS (ESI): *m/z* 789.3 [M]⁺.

The iron(IV) complex **6a** was prepared from (BPFMC)Fe^{III}(OEt₂)₂ by a method similar to that used for preparation of **4a** from its iron(III) complex [21]. Thus, 50 mg (0.05 mmol) of (BPFMC)Fe^{III}(OEt₂)₂ was dissolved in 30 mL of CH₂Cl₂. The resulting mixture was washed twice with HCl (10%) and with water. During the acidic washing, the color of the mixture changed from red-brown to deep brown. The solution was dried over Na₂SO₄, and the solvent was removed under vacuum. Recrystallization of the precipitated solid from benzene/heptane gave 38 mg (0.045 mmol, 90 %) of (BPFMC)Fe^{IV}Cl. UV-visible (CH₃CN) λ_{max}, nm (log ε), 364 (4.30), 390 (4.56). ¹H NMR (CD₃CN): δ 24.84 (s, 1H), 24.60 (s, 1H), 10.84 (d, 4H), 4.07 (s, 3H), –0.55 (s, 1H), –3.00 (s, 1H), –3.31 (s, 1H), –17.33 (s, 1H), –38.58 (s, 1H). LRMS (ESI): *m/z* 789.3 [M-H-Cl]⁺.

Corrole-iron(IV) chlorates (**4d** and **6d**) and iron(III) corrole radical cation chlorates (**5d** and **7d**)

The chlorate complexes **4d** and **6d** were prepared *in situ* by rapidly mixing a solution of (Cor) Fe^{IV}Cl (2×10^{-5} M) with an excess amount of Ag(ClO₃) ($2-3 \times 10^{-2}$ M) in CH₃CN at 22 °C. The resulting solutions were immediately analyzed by UV-visible spectroscopy. At room temperature, complexes **4d** and **6d** rapidly rearranged to the corrole radical cation complexes **5d** and **7d**. Spectral details for these compounds are collected in Table 2.

Corrole-iron(IV) nitrates (**4b** and **6b**)

The stable nitrate complexes were prepared by stirring an equivalent amount of silver nitrate (AgNO₃) ($2-3 \times 10^{-5}$ M) with **4a** or **6a** ($2-3 \times 10^{-5}$ M) in CH₃CN for 15 min at 22 °C. The mixtures were filtered and used immediately for further studies. Spectral details for these compounds are listed in Table 2.

The (TPFC)Fe^{IV}(NO₃) complex was isolated from CH₃CN and analyzed: Anal.: calcd for C₃₇H₈F₁₅FeN₅O₃•H₂O: C 47.82, H 1.08, N 7.54; found: C 47.59, H 1.22, N 7.87.

(TPFC)Fe^{IV}(OTs) (**4c**) and (TPFC)[•]Fe^{III}(OTs) (**5c**)

The metastable tosylate complex **4c** was prepared by stirring a solution of **4a** (2×10^{-5} M) with an equivalent amount of silver tosylate in CH₃CN at 22 °C for 15 min. Filtration gave a solution containing **4c** that slowly reacted to give complex **5c**. Spectral details for these compounds are in Table 2.

Instrumentation

UV-visible spectra were recorded on an Agilent 8453 diode-array spectrophotometer. Room temperature stopped-flow mixing studies were performed on an RX2000 rapid kinetics spectrometer accessory (Applied Photophysics) coupled with the above spectrometer. Variable temperature kinetics were measured on an Ocean Optics USB4000 spectrometer with a thermostated reaction cell holder that was cooled with circulating coolant from a temperature-controlled bath; temperatures were measured with a thermocouple placed adjacent to the cell in the cell holder. ¹H NMR spectra were recorded in deuterated solvents on a Bruker Advance DRX-500 (500 MHz) instrument with digital sample-temperature control unit. Chemical shifts (δ) are reported in parts per million (ppm) relative to tetramethylsilane (TMS, δ = 0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet), numbers of hydrogen atoms, and peak assignment. X-band EPR spectra were obtained at 77 K on a Varian E109E spectrometer.

EPR spectroscopic studies

EPR spectra were collected with the following conditions: sample concentration, 5 mM; central magnetic field, 4000 G; scan width, 8000 G; modulation amplitude, 4 G; gain, $1.25 \times 1000 \times 10$; microwave frequency, 8.89 GHz; microwave power 1 mW; scan time, 240 s; sample temperature, 77 K.

For complexes **2**, a solution of 40 mM Fe(ClO₄)₃ in CH₃CN was freshly prepared. A solution of complex **2** (5 mM) in CH₃CN was cooled to -40 °C, and 1.1 equivalent of Fe(ClO₄)₃ was added with vigorous mixing. The color changed quickly from red to brown (**2a**) or dark purple (**2b**). The mixture was rapidly transferred to a cooled EPR tube with a pre-cooled pipette, and the tube was sealed with a septum cap and freeze-quenched in liquid nitrogen. Upon warming, these solutions changed to a green color.

For corrole-iron(IV) chlorate complex **4d**, a solution of 4 mM (TPFC)Fe^{IV}Cl in CH₃CN was prepared and cooled to −40 °C before 2–3 equivalents of AgClO₃ was added with vigorous mixing. The EPR spectrum was obtained as above. Upon warming, the solution changed color from green to brown. The relatively stable corrole-iron(IV) tosylate **4c** was prepared at room temperature from reaction of **4a** in CH₃CN (4 mM) with 1–2 equivalents of AgOTs.

NMR and magnetic susceptibility studies

For both ¹H NMR and magnetic susceptibility studies, samples of **2a** and **2b** were prepared as described above for the EPR studies with the exceptions that 1.0 equivalents of Fe(ClO₄)₃ was used, CD₃CN was the solvent, NMR tubes were used, and the samples were maintained at −40 °C after mixing. After the spectra of **2a** and **2b** were acquired, the samples were warmed to room temperature and then cooled to −40 °C again for spectral acquisition that confirmed formation of **3a** and **3b**. In the magnetic susceptibility studies, a coaxial tube containing neat CD₃CN was used, and the magnetic susceptibility was measured for the ¹H signal of CHD₂CN with a narrow window (−5 to 5 ppm). NMR experiments were attempted with **2c**, but the spectrum obtained at low temperature was the same as that of authentic **3c**.

For corrole complexes **4b**, **4c**, and **5c**, the stable complexes were prepared in a vial, and AgCl was removed by filtration into an NMR tube. For unstable species, **5d** and **5e**, the samples were prepared in an NMR tube, and the AgCl was not filtered from the solution.

Results and Discussion

Metastable porphyrin iron(IV) diperchlorate species

The porphyrin (Por) complexes studied in this work are shown in Chart 1. 5,10,15,20-Tetraphenylporphyrin (TPP), 5,10,15,20-tetramesitylporphyrin (TMP), and 2,3,7,8,12,13,17,18-octaethylporphyrin (OEP) macrocycles were employed. Iron complexes of these macrocycles are well known, and (Por)Fe^{III}(Cl) are commercially available or readily prepared. We exchanged the chloride ligand with perchlorate by reaction of the chloride complex with Ag(ClO₄) to give complexes **1** so that the identity of ligands on the metal in the more highly oxidized species would not be an issue [29,30].

Oxidation of complexes **1** can occur on the metal to give the iron(IV) “neutral” porphyrins **2** or the iron(III) porphyrin radical cations **3**. For each of the systems studied here, oxidation in methylene chloride solution with ferric perchlorate, Fe(ClO₄)₃, has been reported to give the iron(III) radical cations **3** [23,29,30]. Ferric perchlorate is more soluble in acetonitrile than in methylene chloride. When oxidation reactions were conducted in acetonitrile solvent at low temperature, the first-formed product was the iron(IV) porphyrin species **2**. Compounds **2** were metastable and rapidly rearranged at room temperature to give the known products **3**. For the TPP and TMP systems, transients **2a** and **2b** were characterized by spectroscopic methods (UV-visible, EPR and ¹H NMR spectroscopies) and magnetic susceptibility studies. The OEP derivative **2c** appeared to convert to **3c** at 22 °C with a rate similar to those for conversions of **2a** and **2b** as determined by kinetic UV-visible spectroscopy, but our attempts to detect **2c** by NMR spectroscopy at low temperature were not successful.

Isolations of metastable species **2** were not possible because the species rearranged rapidly, often in seconds, at low temperatures. Dissociation and reassociation of a perchlorate anion in **2** is expected, and we cannot exclude the possibility that species **2** predominantly exists as a charged complex with iron bound to only one perchlorate group. Nonetheless, when the samples of **2** were warmed gradually, the diperchlorate complexes **3** were the only species detected from reactions of **2**.

In UV-visible spectral studies, solutions of compounds **1** in CH₃CN were mixed rapidly at room temperature with CH₃CN solutions containing an excess of Fe(ClO₄)₃. The spectra of compounds **1–3** are collected in Table 1. Spectra of the iron(III) porphyrin complexes **1** and iron(III) porphyrin radical cations **3** in methylene chloride or chloroform were previously reported [23,29,30], and those for species **1** and **3** in acetonitrile were similar. The spectra of the iron(IV) complexes **2** differed in a predictable manner. The Soret bands for compounds **2** were sharp peaks, and the molar extinction coefficients were greater than those of **1**, whereas the Soret bands for **3** were broader and less intense. The Q-bands were characteristic, especially the Q-band for the porphyrin radical cation complexes **3**, which had a broad long wavelength absorbance in the range 600–750 nm. Figure 1 shows the spectra for the TMP system.

The ¹H NMR spectra in the TPP and TMP series also suggested the identity of the iron(IV) species. ¹H NMR spectra in CD₂Cl₂ or CDCl₃ solutions were reported previously for compounds **1a** [33], **3a** [34], **1b** [23], **3b** [23], **1c** [28] and (OEP)⁺Fe^{III}(Cl)(ClO₄) [29]. We confirmed the identity of compounds **1** and **3** by obtaining ¹H NMR spectra in CD₂Cl₂ solutions and in CD₃CN solutions, which were similar (Table 1). For the TPP and TMP series, NMR spectra of the metastable complexes **2a** and **2b** also were obtained. When the iron(III) porphyrin complexes in CD₃CN solutions cooled to –40 °C were treated with 1 equivalent of Fe(ClO₄)₃, new NMR signals formed that were attributed to transients **2a** and **2b**. When the samples were warmed to room temperature and again cooled to –40 °C, the NMR spectra of complexes **3a** and **3b** were observed. The characteristic features of these spectra were that compounds **1** had relatively sharp signals, the signals from compounds **2** were quite broad, and the signals from compounds **3** were again relatively sharp. Figure 2 shows the results for the (TMP) complexes **1b**, **2b**, and **3b**. We specifically note that species **2a** and **2b** were expected to have very small, upfield signals in their ¹H NMR spectra at $\delta \approx -30$ for pyrrole protons (see ref [23] for an example). Unfortunately, the NMR spectra of **2a** and **2b** at –40 °C contained only broad signals (cf. Figure 2), and we could not detect any upfield signals.

For EPR spectroscopic studies, samples of compounds **2a** and **2b** were prepared in CH₃CN at –40 °C, and the samples were cooled to 77 K. The EPR spectra contained small signals from residual starting compounds **1**, but no new signals for compounds **2** were observed. Integration of the signals from compounds **1** indicated that more than 80% of the material had been converted to EPR silent species. The iron(IV) species **2** were expected to be EPR silent because they have $S = 1$ [35].

Magnetic susceptibility studies also were performed with samples of **2a** and **2b** using the Evans NMR method [36,37]. The samples were prepared in CD₃CN at –40 °C in NMR tubes containing a coaxial tube with neat CD₃CN solvent. The chemical shift differences in the signals from CHD₂CN in the solvent were measured, and the effective magnetic moment (μ_{eff}) was calculated from the chemical shift differences [37]. At –40 °C, the effective magnetic moments of **2a** and **2b** were $\mu_{\text{eff}} = 2.96 \mu_{\text{B}}$ and $\mu_{\text{eff}} = 3.03 \mu_{\text{B}}$, respectively, where we estimate the errors to be $\pm 10\%$. These values are close to the value expected for an $S = 1$ species ($\mu_{\text{eff}} = 2.83 \mu_{\text{B}}$) [38]. When the samples were warmed, the μ_{eff} values increased as increasing amounts of species **3** were formed. The samples of **3** were cooled to –40 °C again, and NMR spectra were obtained to determine the values of μ_{eff} under the same conditions as used for the samples of **2**, which gave $\mu_{\text{eff}} = 5.50 \mu_{\text{B}}$ for **3a** and $\mu_{\text{eff}} = 5.95 \mu_{\text{B}}$ for **3b**, values consistent with uncoupled spin-admixed iron(III) ($S = 3/2, 5/2$) and porphyrin radical ($S = 1$) [38]. Note that any contribution to the magnetic susceptibility from the by-products of the ferric perchlorate will be constant in these measurements, and the difference in values before and after warming results only from the isomerization of **2** to **3**.

Corrole iron(IV) species

The corrole (Cor) species studied in this work are shown in Chart 2. The corrole systems were 5,10,15-*tris*(pentafluorophenyl)corrole (TPFC) and 5,15-*bis*(pentafluorophenyl)-10-*p*-methoxyphenylcorrole (BPFMC). Isomers **4** and **6** are iron(IV) species with “neutral” corrole ligands (actually corrole tri-anions), and isomers **5** and **7** are iron(III) species with corrole “radical cations” (actually corrole di-anion radicals). Note that neutral corroles have three acidic protons on nitrogen atoms whereas porphyrins have two; therefore fully deprotonated corrole-iron complexes with the metal in a formal +4 oxidation state have a single associated anion and are inherently more stable than porphyrin species with the metal in the +4 oxidation state.

The starting points for the corrole-iron species were the corrole-iron(IV) chlorides **4a** and **6a**, which were formed by air oxidation of the corresponding corrole-iron(III) complexes in the presence of HCl [39]. The chloride counterions in **4a** and **6a** were exchanged by reaction with various silver salts to give nitrate, tosylate, chlorate, and perchlorate derivatives [9].

The structures of formal +4 iron-corrolates have been an issue in recent years [21,40]. Either the iron(IV) trianionic corrole structures or the iron(III) corrole dianion radical structures are possible. The former is an $S = 1$ species, and the latter is an $S = 3/2$ iron-center that could have the macrocycle radical antiferromagnetically coupled to the unpaired electrons on iron [38]. As such, both structures could be EPR silent, and both could have similar effective magnetic moments of $\mu_{\text{eff}} \approx 3 \mu_{\text{B}}$. Differentiation between the two structures is possible from UV-visible and NMR spectral data and from computational results.

In our studies, we relied primarily on UV-visible spectra with support from ^1H NMR spectroscopy for assignment of the corrole-iron species electronic structures. Figure 3 shows typical results for the chlorate isomers in both series of corroles studied. The iron(IV) neutral corrole species have a relatively sharp Soret absorbance and quite weak or absent visible-band absorbances [39,41]. The iron(III) corrole radical cations have broader, less intense Soret bands that are blue-shifted from the iron(IV) species and weak but obvious long wavelength absorbances ($\lambda_{\text{max}} \approx 650 \text{ nm}$) that are characteristic of radicals in highly conjugated systems.

^1H NMR spectra could be obtained for some of the (TPFC)-iron derivatives, and these provided supporting evidence for the structure assignments. NMR chemical shifts in corrole-iron(IV) derivatives have been shown to be highly variable for different ligands on iron [42], but the NMR spectra we obtained demonstrated similarities for the corrole-iron(IV) species (three upfield peaks) and for the corrole-iron(III) radical cations (four upfield peaks) as listed in Table 2. The NMR spectra also clearly demonstrate when an isomerization occurs as shown in Figure 4, which contains the spectra of the initially-formed metastable (TPFC)-iron(IV) tosylate (**4c**) and its isomerization product **5c**.

The formal +4 iron-(TPFC) chloride complex **4a** was initially prepared by Gross who assigned the structure **4a** [39]. In our preparative reactions, we employed **4a** in CH_3CN solutions. The species was EPR silent, and the effective magnetic moment measured in CD_3CN solution at 22°C by the Evans method [36] was $\mu_{\text{eff}} = 2.87 \mu_{\text{B}}$; both features are consistent with structure **4a**, which has $S = 1$, or structure **5a** ($S = 3/2$) if there is antiferromagnetic coupling of the radical with the iron electrons to give $S = 1$. The ^1H NMR spectrum in CD_3CN and UV-visible spectrum in CH_3CN were similar to those reported [39] for **4a** in CD_2Cl_2 and CH_2Cl_2 solutions, respectively (Table 2). Reactions of complex **4a** with silver salts to exchange the anion gave different results as a function of the new counterion that was exchanged for chloride. The primary methods for structure assignments for the products of these reactions were UV-visible spectra and ^1H NMR spectra (Figures 3 and 4); both types of spectra showed characteristic differences for the two electronic isomers as discussed above.

Reaction of **4a** with Ag(NO₃) at 22 °C gave a species that we assign as structure **4b** on the basis of its UV-visible (Table 2) and ¹H NMR spectra (Figure 4). Importantly, the UV-visible spectrum lacked the highly characteristic long wavelength absorbance due to a radical in the corrole macrocycle [39,41]. Species **4b** was stable when warmed to room temperature.

Reactions of complex **4a** with Ag(ClO₃) at -20 °C and with AgOTs (Ts = tosyl = *p*-CH₃C₆H₄SO₂) at 22 °C in CH₃CN gave metastable species that rearranged at room temperature. The spectral properties of both isomers are listed in Table 2. In both cases, the first-formed species had UV-visible spectra with sharper, more intense Soret bands than their isomers and lacked a long wavelength Q-band absorbance at ca. 650 nm, whereas both isomers that formed upon warming displayed long wavelength Q-band absorbances. From these spectral properties, we assign the first-formed species as iron(IV) corrolates **4c** and **4d**, and the species that formed upon warming as iron(III) corrole radical cations **5c** and **5d**. The ¹H NMR spectra of the tosylate derivatives support the structural assignment (Figure 4). For the iron (IV) species **4c**, the ¹H NMR spectrum was similar to that of the iron(IV) chloride complex **4a**. For the isomerized compounds **5c** and **5d**, the ¹H NMR spectra displayed four distinct upfield signals for the four unique corrole ring protons.

When chloride complex **4a** was allowed to react with Ag(ClO₄) at -20 °C, the initially formed species was stable when warmed to room temperature. In this case, the UV-visible spectrum indicated that the product was the iron(III) corrole radical cation **5e** (Table 2). If iron(IV) corrolate **4e** was formed in the initial exchange reaction, it isomerized to **5e** too rapidly for detection in our method.

The chemistry of the (BPFMC)-iron species **6** and **7** was similar to that of the (TPFC)-iron species as deduced from UV-visible spectra. The iron(IV) chloride complex **6a** was prepared by air oxidation of the iron(III) corrole complex in the presence of HCl. Reaction of chloride complex **6a** with AgNO₃ gave the iron(IV) complex **6b** that did not rearrange on standing. Reaction of **6a** with Ag(ClO₃) at low temperature gave the iron(IV) complex **6d** that rearranged to the iron(III) corrole radical cation **7d** when warmed to room temperature.

The thermodynamically favored electronic isomers for the corrole complexes studied apparently are determined by the counterion binding strengths [43,44]. The iron(IV) corroles are favored with the relatively strong binding chloride and nitrate ligands (**4a**, **4b**, **6a**, **6b**). For the weaker binding ligands OTs, ClO₃, and ClO₄, the iron(III) radical cations are the thermodynamically favored species (**5c**, **5d**, **5e**, **7d**).

Isomerizations of iron(IV) macrocycles to iron(III) macrocycle radical cations

In total, six of the iron(IV) complexes prepared in this work isomerized to their iron(III) macrocycle radical cations, the three porphyrin-iron(IV) diperchlorates (**2a**, **2b**, and **2c**), (TPFC)Fe^{IV}(OTs) (**4c**), (TPFC)Fe^{IV}(ClO₃) (**4d**), and (BPFMC)Fe^{IV}(ClO₃) (**6d**). For these metastable iron(IV) species, the barriers for isomerizations to the thermodynamically favored iron(III) macrocycle radical cation species are of special interest because similar barriers might be involved in the isomerizations of macrocycle-iron(V)-oxo species to iron(IV)-oxo macrocycle radical cations.

Isomerizations of the iron(IV) species to their iron(III) macrocycle radical cations were readily observed by UV-visible spectroscopy. For example, the time-resolved spectra in Figure 3 show conversions of corrole-iron(IV) chlorates **4d** and **6d** to the corrole radical cation iron(III) chlorates **5d** and **7d**, respectively. Nonetheless, the kinetics of the isomerizations reactions could not be analyzed in a straightforward manner because the mechanisms of the isomerizations reactions appear to be highly complex. The difficulty in analyzing the results is illustrated in Figure 5, where, for demonstration purposes, we solved the kinetic data for the

isomerization reactions as first-order processes. Figure 5A shows variable temperature results for reaction of the corrole-iron(IV) chlorate **4d**. The data appears to fit an analysis in the context of Arrhenius theory, but the apparent activation parameters are nonsensical. Specifically, the reaction appears to have a very low activation energy of $E_a = 5.6$ kcal/mol, which is possible, but also an extraordinarily negative entropy term, $\log A = 3$, which gives $\Delta S^\ddagger \approx -50$ eu. Even more problematical from a mechanistic standpoint, when the initial concentrations of iron(IV) species were varied in a series of reactions at constant temperature, the apparent first-order rate constants for isomerizations increased as a fractional order of the iron reactant. Figure 5B shows apparent first-order rate constants for conversion of corrole-iron(IV) species **4d** to **5d** and for conversion of porphyrin-iron(IV) species **2b** to **3b** in log-log format. If the reactions were first-order in iron species, the slopes of these plots would be zero. Instead, both plots have slopes of ca. 0.5, indicating that the iron species are reacting with apparent molecular order of 1.5.

Various mechanistic schemes might be envisioned to rationalize the kinetic results, but it is apparent that detailed studies will be required to understand the reactions well. Until such information is available, we believe it is prudent to discuss the kinetics in terms of half-lives for reactions under similar conditions as opposed to rate constants. The half-lives for isomerizations of the iron(IV) complexes at ca. 1×10^{-5} M in acetonitrile at room temperature are listed in Table 3. For the porphyrin-iron(IV) species, the reactivity is **2b** > **2a** $\approx$ **2c**, but all of the reactions had similar rates, with half-lives of about 10 s at room temperature corresponding to a barrier of $\Delta G^\ddagger \approx 19$ kcal/mol. For the corrole-iron(IV) species, chlorate **4d** reacted much faster than tosylate **4c**, which had a barrier to isomerization of $\Delta G^\ddagger \approx 22$ kcal/mol, indicating an expected trend that the iron(IV) species is increasingly favored by stronger π -donating ligands [43,44]. Interestingly, the changes in electron demand of the macrocycles for the two corrole-iron(IV) chlorates **4d** and **6d** had only a slight effect on the rates of isomerization, which is similar to the small macrocycle effect observed with the porphyrin-iron(IV) species.

Conclusion

Oxidation of porphyrin-iron(III) complexes by ferric perchlorate occurs initially on the metal ion to give metastable porphyrin-iron(IV) diperchlorates, and stable and metastable corrole-iron(IV) complexes can be produced from the corrole-iron(IV) chloride by ligand exchange. Macrocycle iron(IV) complexes with oxygen-bound ligands such as nitrate, chlorate and perchlorate are attractive intermediates because they are photo-labile and react to give high-valent iron-oxo derivatives [9,16], and the methods studied here are expected to be generally useful for preparation of precursors for such photochemical studies. Rearrangements of the metastable iron(IV) species to their iron(III) macrocycle radical cation isomers are fast in some cases, but the lifetimes of the iron(IV) species often are long enough to permit some spectroscopic studies. The rates of rearrangement were found to be relatively insensitive to changes in the macrocyclic ligand substitution but strongly sensitive to the binding strength of the “fifth” ligand to iron. The isomerization rates for the iron(IV) species studied here might be related to the rates of isomerizations of higher valent iron-oxo species and suggest that appreciable barriers for electronic isomerizations of formal +5 iron species are possible.

Acknowledgements

This work was supported by a grant from the National Institutes of Health (GM-48722).

Abbreviations

Cor
corrole

Por	porphyrin
TPP	5,10,15,20-tetraphenylporphyrin or -porphyrinato
TMP	5,10,15,20-tetramesitylporphyrin or -porphyrinato
OEP	2,3,7,8,12,13,17,18-octaethylporphyrin or -porphyrinato
TPFC	5,10,15- <i>tris</i> (pentafluorophenyl)corrole or -corroloto
BPFMC	5,15- <i>bis</i> (pentafluorophenyl)-10- <i>p</i> -methoxyphenylcorrole or -corroloto
LRMS	low resolution mass spectrometry
ESI	electrospray ionization
TMS	tetramethylsilate

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Figure 1. UV-visible spectra for (TMP)Fe^{IV}(ClO₄)₂ (**2b**) (solid line) and (TMP)⁺Fe^{III}(ClO₄)₂ (**3b**) (dashed line) in acetonitrile.

Figure 2.

^1H NMR spectra in CD_3CN at $-40\text{ }^\circ\text{C}$ of $(\text{TMP})\text{Fe}^{\text{III}}(\text{ClO}_4)$ (**1b**), $(\text{TMP})\text{Fe}^{\text{IV}}(\text{ClO}_4)_2$ (**2b**), and $(\text{TMP})^+\text{Fe}^{\text{III}}(\text{ClO}_4)_2$ (**3b**). The relative intensities of the spectra are the same.

Figure 3.

Time-resolved UV-visible spectra of corrole-iron chlorates. **(A)** (TPFC)Fe^{IV}(ClO₃) (**4d**) converting to (TPFC)⁺•Fe^{III}(ClO₃) (**5d**) at ambient temperature; the time slices are at 0.3, 15, 20, 31, 40, and 60 s. **(B)** (BPFMC)Fe^{IV}(ClO₃) (**6d**) converting to (BPFMC)⁺•Fe^{III}(ClO₃) (**7d**) at ambient temperature; the time slices are at 0.3, 7, 18, 23, and 60 s.

Figure 4.
 ^1H NMR spectra of **4c** and **5c** in CD_3CN recorded at 22 °C.

Figure 5.

Kinetic plots. **(A)** Temperature-dependent rate constants for reaction of corrole-iron(IV) chlorate **4d** in acetonitrile; the kinetic values used are apparent first-order rate constants for reactions of 1×10^{-5} M solutions. **(B)** Concentration dependence of apparent first-order rate constants for reactions at room temperature for corrole-iron(IV) chlorate **4d** (solid circles) and porphyrin-iron(IV) perchlorate **2b** (open circles).

1 **2** **3**

- a:** $R_1 = C_6H_5$, $R_2 = H$; (TPP)
b: $R_1 = 2,4,6-(CH_3)_3C_6H_2$, $R_2 = H$; (TMP)
c: $R_1 = H$; $R_2 = C_2H_5$; (OEP)
 $X = (ClO_4)$

Chart 1.

4: $\text{Ar}_1 = \text{Ar}_2 = \text{C}_6\text{F}_5$

5: $\text{Ar}_1 = \text{C}_6\text{F}_5$, $\text{Ar}_2 = \text{C}_6\text{H}_4\text{OCH}_3$

6: $\text{Ar}_1 = \text{Ar}_2 = \text{C}_6\text{F}_5$

7: $\text{Ar}_1 = \text{C}_6\text{F}_5$, $\text{Ar}_2 = \text{C}_6\text{H}_4\text{OCH}_3$

a: $\text{X} = \text{Cl}$; **b:** $\text{X} = \text{NO}_3$; **c:** $\text{X} = \text{SO}_3\text{C}_6\text{H}_4\text{CH}_3$;

d: $\text{X} = \text{ClO}_3$; **e:** $\text{X} = \text{ClO}_4$

Chart 2.

Table 1

Properties of iron-porphyrin complexes.

Complex	UV-visible (nm) ^a	¹ H NMR (δ) ^b	μ _{eff} (μ _B) ^c
(TPP)Fe ^{III} (ClO ₄) (1a)	398 (5.11), 532	74.6, 18.3, 11.9, 11.7	
(TMP)Fe ^{III} (ClO ₄) (1b)	399 (5.07), 530	8.4, 3.6, 2.6, -26	
(OEP)Fe ^{III} (ClO ₄) (1c)	376 (4.92), 503, 553, 634, 559	47.0, 8.3	
(TPP)Fe ^{IV} (ClO ₄) ₂ (2a)	396 (5.14), 532	69.6, 31.6, 16.9	2.96
(TMP)Fe ^{IV} (ClO ₄) ₂ (2b)	397 (5.12), 530	66, 32, 14	3.03
(OEP)Fe ^{IV} (ClO ₄) ₂ (2c)	391 (5.02), 495, 618		
(TPP) ⁺ Fe ^{III} (ClO ₄) ₂ (3a)	393 (5.03), 535, 602, 682	61.8, 32.8, -11.1, -14.2	5.50
(TMP) ⁺ Fe ^{III} (ClO ₄) ₂ (3b)	392 (4.98), 498, 605, 680	92, 71.7, 31.4, 20.8	5.95
(OEP) ⁺ Fe ^{III} (ClO ₄) ₂ (3c)	374 (4.85), 502, 595, 648	69.8, 26.9	5.20

^aUV-visible spectral absorbances in CH₃CN; log ε of the Soret band in parentheses.^bNMR spectra in CD₃CN solution at -40 °C.^cEffective magnetic moment determined in CD₃CN at -40 °C.

Table 2
Properties and magnetic moments of Iron-Corrole Complexes

Complex	UV-vis (nm) ^a	¹ N NMR (δ) ^b	μ _{eff} (μ _B) ^c
(TPFC)Fe ^{IV} Cl (4a)	367 (4.31), 394 (4.60)	3.8, -5.9, -17.1, -49.9 (-20 °C) 4.1, -2.8, -11.6, -36.8	2.87
(TPFC)Fe ^{IV} (NO ₃) (4b)	396 (4.61)	-4.3, -20.4, -47.2	2.89
(TPFC)Fe ^{IV} (OTs) (4c)	397 (4.63)	-5.0, -13.4, -45.9	2.85
(TPFC)Fe ^{IV} (ClO ₃) (4d)	397 (4.65)		2.87
(TPFC) ⁺ Fe ^{III} (OTs) (5c)	379 (4.61), 647	-3.3, -21.9, -48.0, -52.8	2.90
(TPFC) ⁺ Fe ^{III} (ClO ₃) (5d)	380 (4.55), 650	-4.7, -9.9, -22.4, -61.2 (-20 °C)	2.95
(TPFC) ⁺ Fe ^{III} (ClO ₄) (5e)	378 (4.53)		
(BPFMC)Fe ^{IV} Cl (6a)	364 (4.30), 390 (4.56)		
(BPFMC)Fe ^{IV} (NO ₃) (6b)	398 (4.64)		
(BPFMC)Fe ^{IV} (ClO ₃) (6d)	394 (4.63)		
(BPFMC) ⁺ Fe ^{III} (ClO ₃) (7d)	381 (4.52)		

^a In CH₃CN at room temperature; log ε values are in parentheses.

^b In CD₃CN at 22 °C unless noted.

^c Effective magnetic moment measured in CD₃CN at 22 °C.

Table 3Observed half-lives for isomerizations of iron(IV) complexes in acetonitrile.^a

Complex	Temp (°C)	<i>t</i> _{1/2} (s)
(TPP)Fe ^{IV} (ClO ₄) ₂ (2a)	22	13
	9	20
	1	28
(TMP)Fe ^{IV} (ClO ₄) ₂ (2b)	22	10
(OEP)Fe ^{IV} (ClO ₄) ₂ (2c)	22	13
(TPFC)Fe ^{IV} (OTs) (4c)	22	2500
(TPFC)Fe ^{IV} (ClO ₃) (4d)	23	15
(BPFMC)Fe ^{IV} (ClO ₃) (6d)	22	18

^aFor isomerizations of ca. 1×10^{-5} M solutions.