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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, $Fe(ClO_4)_3$, 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) toslyate, (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.

1. 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 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

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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].

2. Materials and methods

2.1. 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 preformed by Atlantic Microlab, Inc.

2.2. Porphyrin complexes

The macrocycles for the porphyrin (Por) complexes were 5,10,15,20-tetraphenylporphryin (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 $TMPH_2$ free ligand and the (TMP)Fe^{III}Cl complex were prepared by reported methods [26,27]. (TPP)Fe^{III}(ClO_4) (**1a**), (TMP)Fe^{III}(ClO_4) (**1b**), and (OEP)Fe^{III}(ClO_4) were prepared by reported methods [23,26–28]. Authentic samples of $(TPP)^{+\cdot}Fe^{III}(ClO_4)_2$ (**3a**), $(TMP)^{+\cdot}Fe^{III}(ClO_4)_2$ (**3b**), and $(OEP)^{+\cdot}Fe^{III}(ClO_4)_2$ (**3c**) were prepared by reported methods [23,29,30].

2.3. Porphyrin-iron(IV) diperchlorate complexes (**2**)

In a typical reaction, solutions of **1a** (20 μM in CH_3CN) and $Fe(ClO_4)_3$ (0.5 mM in CH_3CN) 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.

2.4. 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 $(TPFC)H_3$ and $(BPFMC)H_3$ were prepared according to reported methods [31,32]. $(TPFC)Fe^{III}(Et_2O)_2$ 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.

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

The procedure described for insertion of iron into the (TPFC) ligand [21] was used to prepare $(BPFMC)Fe^{III}(OEt_2)_2$. 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 $(BPFMC)Fe^{III}(OEt_2)_2$ (75 mg, 0.08 mmol, 80%). UV–visible (CH_3CN): λ_{max}, nm (log ε), 406 (4.75), 550 (1.58). ^1H NMR ($CDCl_3$): 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 $(BPFMC)Fe^{III}(OEt_2)_2$ 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)-$Fe^{III}(OEt_2)_2$ was dissolved in 30 mL of CH_2Cl_2. 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 Na_2SO_4, 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 (CH_3CN) λ_{max}, nm (log ε), 364 (4.30), 390 (4.56). ^1H NMR (CD_3CN): 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 $[M-H-Cl]^+$.

2.6. 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 $Ag(ClO_3)$ ($2–3 \times 10^{-2}$ M) in CH_3CN 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.

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

The stable nitrate complexes were prepared by stirring an equivalent amount of silver nitrate ($AgNO_3$) ($2–3 \times 10^{-5}$ M) with **4a** or **6a** ($2–3 \times 10^{-5}$ M) in CH_3CN 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}(NO_3) complex was isolated from CH_3CN and analyzed: Anal. calcd for $C_{37}H_8F_{15}FeN_5O_3 \cdot H_2O$: C 47.82, H 1.08, N 7.54; found: C 47.59, H 1.22, N 7.87.