

Direct Incorporation of a Ferric Ion in the Porphyrinogen Core: Tetrakis(cyclohexyl)iron Porphyrinogen Anion with Different Conformers and Its Reaction with Iodine

Dibyendu Bhattacharya, Soumen Dey, Suman Maji, Kuntal Pal, and Sabyasachi Sarkar*

Department of Chemistry, Indian Institute of Technology, Kanpur 208 016, India

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$\text{Et}_4\text{N}[\text{L}''\text{Fe}^{\text{III}}]\cdot 3\text{DCM}$ (**1**) is directly synthesized by adding ferric chloride into a solution of a lithium salt of tetrakis(cyclohexyl)porphyrinogen (L''). $[\text{L}'']^{4-}$ is a good chelating ligand for both $\text{Fe}(\text{III})$ and $\text{Fe}(\text{II})$ ions. It is an avid proton scavenger but not a reducing agent. **1** showed a magnetic moment (μ_{eff}) of $4.3 \mu_{\text{B}}$ in the solid, which changed to $6.0 \mu_{\text{B}}$ in solution. This change in spin state is common for all iron porphyrinogens. **1** showed polymorphism, and with pyridine in the lattice, it changed to $\text{Et}_4\text{N}[\text{L}''\text{Fe}^{\text{III}}]\cdot \text{DCM}_{0.5}\text{Py}_{1.5}$ (**2**), possessing two different conformers. Calculation of these conformers at the density functional theory level showed the relative energies of all d orbital changes in three conformers, highlighting the influence of the disposition of a peripheral ligand. Iodine oxidation of **1** yielded $[\text{L}''^{\Delta\Delta}\text{Fe}^{\text{II}}][\text{I}_3\cdot\text{I}_2^+\cdot\text{I}_3^-]$ (**3**) with the introduction of two $\text{C}_\alpha\text{--C}_\alpha$ bonds with concomitant reduction of $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$. Its μ_{eff} ($5.4 \mu_{\text{B}}$) in the solid changed to $4.8 \mu_{\text{B}}$ in solution, suggesting a high spin state ($S = 2$) for $\text{Fe}(\text{II})$.

Ferrous is known to be the effective oxidation state of iron for its incorporation in the biosynthesis of heme.^{1a} In the synthesis of iron porphyrin, it was shown that it is $\text{Fe}(\text{II})$ that is incorporated into porphyrin to make room for introduction of $\text{Fe}(\text{III})$.^{1b} The metalation of *meso*-octaalkylporphyrinogen has been shown to follow a similar trend.^{2a} The introduction of iron into the core of *meso*-octaalkylporphyrinogen has been carried out several times, and in each case, it was stated that an excess of ferrous ions would lead to the formation of iron(III) porphyrinogen.

The synthesis of $\text{Li}_2(\text{THF})_4\text{LFe}^{\text{II}}$ has been reported by the reaction between FeCl_2 and $\text{Li}_4\text{L}\cdot 4\text{THF}$ ($\text{L} = \textit{meso}$ -octaeth-

ylporphyrinogen) in 80% yield.³ The use of an excess of FeCl_2 led to the isolation of the *meso*-octaethyliron(III) porphyrinogen complex³ similar to the structurally characterized $[\text{Li}(\text{MeCN})][\text{L}'\text{Fe}^{\text{III}}]$ ($\text{L}' = \textit{meso}$ -octamethylporphyrinogen) complex, where the stoichiometry between L' and FeCl_2 as 1:2 was used.⁴ This was thought to be a disproportionation-type reaction and has recently been shown to be due to the oxidation of $[\text{L}'\text{Fe}(\text{II})]^{2-}$ by an excess of FeCl_2 present in the reaction mixture with the precipitation of elemental iron.⁵ It is reported that direct incorporation of a trivalent late-transition-metal ion like $\text{Fe}(\text{III})$ into the porphyrinogen core is not possible.^{2b}

In contrast to the behavior of iron porphyrin^{1b} and the earlier prediction on the direct nonincorporation of $\text{Fe}(\text{III})$ into the porphyrinogen core,² we report, herein, the synthesis of $\text{Et}_4\text{N}[\text{L}''\text{Fe}^{\text{III}}]\cdot 3\text{DCM}$ (**1**) by directly using a $\text{Fe}(\text{III})$ ion. On the basis of the electrochemistry of **1**, its irreversible ring oxidation was followed using elemental iodine, resulting in the isolation of $[\text{L}''^{\Delta\Delta}\text{Fe}^{\text{II}}][\text{I}_3\cdot\text{I}_2^+\cdot\text{I}_3^-]$ (**3**).

1 was synthesized by adding a stoichiometric amount of anhydrous FeCl_3 into a solution of a lithium salt of tetrakis(cyclohexyl)porphyrinogen (L'') in a THF medium.⁶ X-ray structure analysis of **1** revealed that $\text{Fe}(\text{III})$ has been incorporated into this porphyrinogen core.⁷ Its room-temperature magnetic moment in the solid state has been found to be $4.3 \mu_{\text{B}}$ at 298 K ($3.8 \mu_{\text{B}}$ at 6 K). When magnetic measurement was carried out in DMF or in a DCM medium by NMR,⁸ the spin state of $S = 3/2$ changed to $S = 5/2$, yielding $\mu_{\text{eff}} = 6.0 \mu_{\text{B}}$. This change in the spin state of $S = 3/2$ (in solid) to $S = 5/2$ (in solution) is a general phenomenon observed in all characterized iron(III) porphyrinogen systems.⁹ The space-filling model of **1** showed no room for

* To whom correspondence should be addressed. E-mail: abyaa@iitk.ac.in.

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- (2) (a) Floriani, C.; Floriani-Moro, R. In *The Porphyrin Handbook*; Kadsish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: New York, 2000; Vol. 3, p 389. (b) A hexacoordinated V complex using $\text{V}(\text{III})$ as the starting material has been reported. See: Jubbe, J.; Gambarotta, S. *J. Am. Chem. Soc.* **1993**, 115, 10410–10411.

- (3) (a) Judd, J.; Jacoby, D.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1992**, 31, 1306. (b) A very similar stoichiometric reaction yielded the corresponding $\text{Ru}(\text{II})$ complex. See: Bonomo, L.; Stern, C.; Solari, E.; Scopelliti, R.; Floriani, C. *Angew. Chem., Int. Ed.* **2001**, 40 (8), 1449–1452.
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- (5) Bachmann, J.; Nocera, D. G. *J. Am. Chem. Soc.* **2005**, 127, 4730–4743.
- (6) Detail syntheses of **1–3** are in the Supporting Information.

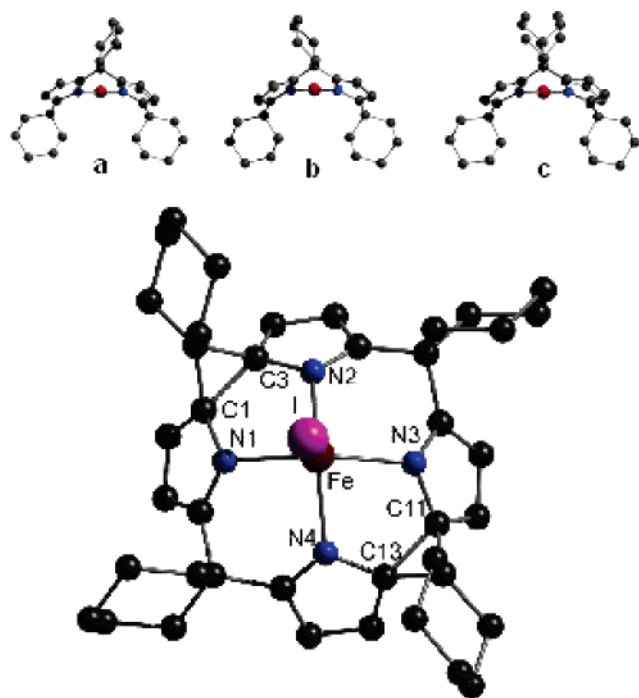


Figure 1. Conformer of the anion of **1** (top, a), conformers of the anion of **2** (top, b and c), and the structure of the anion of **3** (bottom) (see the Supporting Information for ORTEP plots). Color code: C, gray; N, blue; Fe, brown; I, pink.

solvent coordination, which could have been responsible for altering the energy of the $d_{x^2-y^2}$ orbital, resulting in the change in the spin state. Recrystallization of **1** in DCM in the presence of pyridine retained the molecular structure of **1** with the presence of pyridine in the lattice to yield $\text{Et}_4\text{N}[\text{L}''\text{Fe}^{\text{III}}]\cdot\text{DCM}_{0.5}\text{Py}_{1.5}$ (**2**). However, the conformational orientation of the molecules in **2** differed in comparison to that found in **1**. In the asymmetric unit of **2**, the orientations of the two molecules (see Figure 1, top, conformers b and

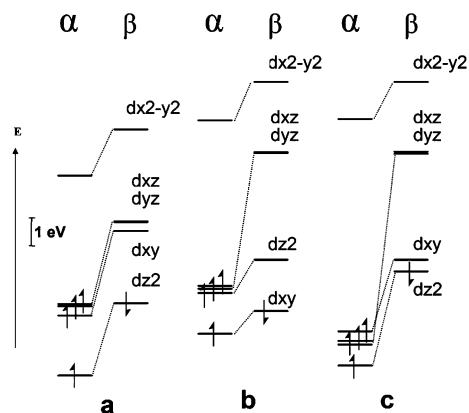


Figure 2. Comparison of molecular orbital energy level diagrams (a–c numbering is identical with that in Figure 1; only d orbitals are shown).

c) were different from each other and from that of the molecule present in **1** (Figure 1, top, conformer a). Density functional theory (DFT) calculation of these conformers showed an interesting perturbation in the molecular orbital energy level (Figure 2). The relative energy levels of all d orbitals change drastically in the three conformers, highlighting the influence of the disposition of a peripheral ligand (flipping of the cyclohexyl ring). The electrostatic surface potentials of all three conformers differ,¹⁰ suggesting the possibility of solvent interaction with **1**, which may affect the conformation of the molecule in such a way as to lower the energy of the $d_{x^2-y^2}$ orbital, resulting in the change in the spin state. Iron incorporation in porphyrin and porphyrinogen does not follow the same chemistry. For porphyrin, its deviation from planarity with out-of-plane displacement of Fe(III) in pentacoordination and planar tetracoordination of Fe(II) and their relative stability even in an aqueous medium suggested that protonated porphyrin does not possess any extra stability. The metalation and demetalation of porphyrin are generally reversible and pH-dependent. In contrast, for porphyrinogen its ligational role toward metal ions is centered on likelihood of the extremely basic tetralithiated $[\text{L}'']^{4-}$ ion, which is an avid proton scavenger, to change to the stable $\text{H}_4\text{L}''$. $[\text{L}'']^{4-}$ is not reducing but a good chelating ligand. The addition of 1 equiv of anhydrous FeCl_2 or FeCl_3 to it resulted in immediate complexation to generate the respective complex anion. The addition of 2,2'-bipyridine or $[\text{Bu}_4\text{N}]_3[\text{Fe}(\text{III})(\text{CN})_6]$ into a solution of $[\text{L}'']\text{Fe}^{\text{II}}^{2-}$ did not show any color changes, confirming the absence of any free or dissociable Fe(II) ion. Similarly, in the case of $[\text{L}'']\text{Fe}^{\text{III}}^{2-}$, the addition of $[\text{Bu}_4\text{N}]_3\text{H}[\text{Fe}^{\text{II}}(\text{CN})_6]$ did not produce any prussian blue precipitate, suggesting that the complexed Fe(III) is not dissociated readily. However, both of the anions are susceptible to hydrolysis (Scheme 1). For the formation of $[\text{L}'']\text{Fe}^{\text{III}}^-$ in the presence of excess FeCl_2 , the reaction involves two redox couples. In THF, the cyclic voltammetric response of the $[\text{L}'']\text{Fe}^{\text{III}}^-/[\text{L}'']\text{Fe}^{\text{II}}^{2-}$ couple is irreversible with E_p at -1.05V vs Ag/AgCl . In the same solvent, the electrochemical response of FeCl_2 showed an irreversible redox response

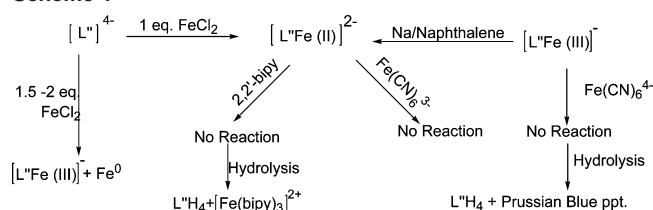
(7) Crystal data for $\text{Et}_4\text{N}[\text{L}'']\text{Fe}^{\text{III}}\cdot 3\text{DCM}$ (**1**): $a = 13.640(5)\text{ \AA}$, $b = 18.548(5)\text{ \AA}$, $c = 20.750(5)\text{ \AA}$, $\alpha = 90(5)^\circ$, $\beta = 90(5)^\circ$, $\gamma = 90(5)^\circ$, $V = 5250\text{ \AA}^3$, orthorhombic, space group $P222$, $Z = 4$, $D_{\text{calc}} = 1.298\text{ g cm}^{-3}$, $T = 100\text{ K}$. Of a total of 35 396 reflections collected, 12 997 were independent ($R_{\text{int}} = 0.049$). Final $R1 = 0.065$ [$I > 2\sigma(I)$], $wR2 = 0.1514$, $\text{GOF} = 0.999$. Crystal data for $\text{Et}_4\text{N}[\text{L}'']\text{Fe}^{\text{III}}\cdot\text{DCM}_{0.5}\text{Py}_{1.5}$ (**2**): $a = 11.696(5)\text{ \AA}$, $b = 16.749(5)\text{ \AA}$, $c = 24.767(5)\text{ \AA}$, $\alpha = 90.663(3)^\circ$, $\beta = 96.540(5)^\circ$, $\gamma = 95.869(5)^\circ$, $V = 4794\text{ \AA}^3$, triclinic, space group $P\bar{1}$, $Z = 2$, $D_{\text{calc}} = 1.266\text{ g cm}^{-3}$, $T = 100\text{ K}$. Of a total of 32 274 reflections collected, 22 809 were independent ($R_{\text{int}} = 0.047$); $\text{GOF} = 1.041$, final $R1 = 0.094$ [$I > 2\sigma(I)$], $wR2 = 0.205$. Crystal data for $[\text{L}'']\text{Fe}^{\text{III}}[\text{I}_3\cdot\text{I}_2^+\cdot\text{I}_3^-]$ (**3**): $a = 11.742(5)\text{ \AA}$, $b = 13.001(5)\text{ \AA}$, $c = 17.686(5)\text{ \AA}$, $\alpha = 85.904(5)^\circ$, $\beta = 72.965(5)^\circ$, $\gamma = 72.100(5)^\circ$, $V = 2456\text{ \AA}^3$, triclinic, space group $P\bar{1}$, $Z = 2$, $D_{\text{calc}} = 2.297\text{ g cm}^{-3}$, $T = 100\text{ K}$. Of a total of 16 338 reflections collected, 11 658 were independent ($R_{\text{int}} = 0.017$); $\text{GOF} = 1.067$, final $R1 = 0.0746$ [$I > 2\sigma(I)$], $wR2 = 0.2199$.

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(9) We follow the synthesis of Fe(III) containing three other porphyrinogen (octaethyl, octamethyl, and methylethyl substituted) using the present synthetic procedure to isolate deep red tetraethylammonium salt of the corresponding iron(III) porphyrinogen. For the octaethylporphyrinogen, Floriani et al. reported a solid-state magnetic moment value of $4.35\text{ }\mu_B$ at 293 K .³ The same complex synthesized by the present method showed the room-temperature magnetic moment $4.35\text{ }\mu_B$, identical to that. However, in DMF, its magnetic behavior changed to that of high-spin Fe(III), showing $\mu_{\text{eff}} = 6.2\text{ }\mu_B$. For iron(III) butylporphyrinogen, the solid-state magnetic moment value was $\mu_{\text{eff}} = 4.05\text{ }\mu_B$ (SQUID measurement), which followed Curie–Weiss law ($\mu_{\text{eff}} = 3.8\text{ }\mu_B$ at 6 K). Upon measurement in DMF, it changes to a high-spin type, showing $\mu_{\text{eff}} = 6.1\text{ }\mu_B$.

(10) Calculations were carried out with the CAChe 5.03 program of Fujitsu Ltd., using a ZINDO semiempirical method.

Scheme 1



around -0.05 V vs Ag/AgCl along with the deposition of the reduced metallic iron on the electrode. The small excess of free Fe(II) in the THF solution of $[L''Fe^{II}]^{2-}$ thus responds to oxidize the complex anion to the relatively more stable Fe(III) species. Because of the difference in the ligational nature between $[L''Fe^{II}]^{2-}$ and the THF-coordinated Fe(II) ion, the observed redox reaction between them may not be classified as the “normal” disproportionation reaction of the transition-metal ions.

1 in other solvents responded with a reversible reduction of Fe(III) in its cyclic voltammogram study followed by an irreversible oxidation of coordinated porphyrinogen. In DCM, the oxidation process is easier ($+0.43$ V vs Ag/AgCl) than that in DMF ($+0.59$ V vs Ag/AgCl). Interestingly, in DCM, two irreversible oxidation processes were observed, and the second one is rather ill-defined and appeared at $+1.2$ V vs Ag/AgCl. It is known that metalated porphyrinogen is capable of oxidation involving $C_\alpha-C_\alpha$ bond formation with apparent two- and four-electron dehydrogenase-type reactions.¹¹ To follow the predicted oxidation of **1** by an electrochemical study, we oxidized **1** in DCM by iodine to isolate the oxidized product **3**. Its X-ray structure confirmed that the porphyrinogen has been oxidized with the introduction of two $C_\alpha-C_\alpha$ bond formations (instead of one) with concomitant reduction of the coordinated Fe(III) to Fe(II), which, in turn, ligated with one iodide ion, resulting in pentacoordination of Fe(II) (Figure 1, bottom).⁷ Oxidation by transition-metal ions such as Cu(II) has extensively been done where the copper cluster anions formed as the byproduct in such a reaction invariably trap the oxidized cationic species.^{2a} A cleaner oxidation was reported with the $[Fe(cp)_2]^+$ cation.⁵ The isolation of **3** suggested that the irreversible redox chemistry must be a complex process. Its room-temperature magnetic moment in the solid showed $\mu_{\text{eff}} = 5.4 \mu_B$, which is higher than that expected for a high spin Fe(II) state ($S = 2$), but in solution (DMF or DCM), its magnetic moment showed a value ($\mu_{\text{eff}} = 4.8 \mu_B$) expected for Fe(II) in a high spin state ($S = 2$). The lattice of **3** possesses a DCM molecule and one I_2 unit along with two I_3^- units. In the solid state at room temperature, this compound showed an EPR signal with g value = $\langle 2.03 \rangle$, which could have originated from an ion pair like $I_2^+I_3^-$. The reduction of the magnetic moment and the loss of the EPR signal in solution are consistent with the disappearance of ion pair

(11) Angelis, S. D.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *J. Am. Chem. Soc.* **1994**, *116*, 5691–5701.

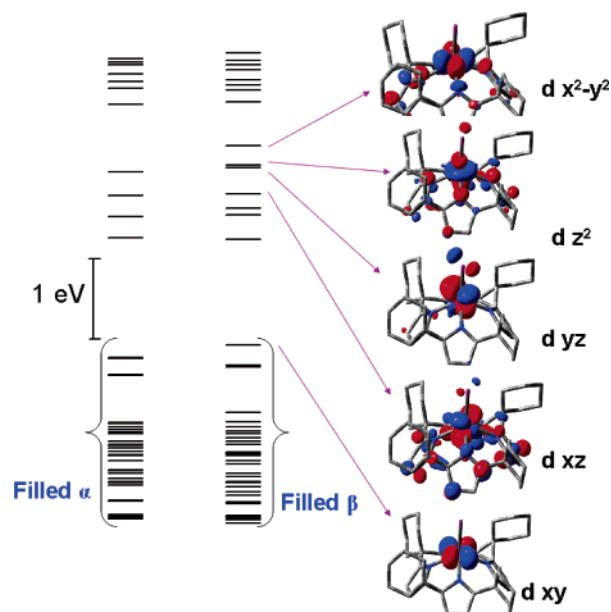


Figure 3. Molecular orbital energy level diagram and frontier molecular orbital plot of d orbitals for **3**.

$I_2^+I_3^-$ interaction.¹² The frontier molecular orbital analysis (Figure 3) showed the population of four unpaired electrons essentially in four d orbitals.^{13,14} A thermogravimetric study of **3** showed that at 164 °C it loses one molecule of DCM and one molecule of I_2 under Ar and above that temperature it is not thermally stable. Oxidation of **1** by iodine in other solvents or by other halogens such as Br_2 or other oxidants behaved differently, and details for these will be published later.

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Supporting Information Available: Details of synthesis, cyclic voltammograms of **1** in different solvents, ORTEP plots with thermal ellipsoids, SQUID magnet measurements for **1** and **3**, complete ref 13, and X-ray crystallographic files for **1–3** (CIF format). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (12) Considering the oxidation state of iron coordinated with one iodide ion, the cation in **3** has a monocationic charge, which requires one I_3^- as a counteranion, leaving formally the I_2^+/I_3^- ion pair in the crystal.
- (13) Pople, J. A.; et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003 (see the Supporting Information).
- (14) DFT calculations have been carried out by employing a B3LYP hybrid functional using the *Gaussian 03* program; molecular orbitals were visualized using G View. The 6-31g** basis set was used for the C, N, and H atoms, and MidiX was used for the I atom; the effective core potential basis set LANL2DZ was used for the Fe atom. The geometry was taken from the crystal structure. Because spin restriction is lifted, there is no common spatial wave function for each α and β spin pair, and two manifolds of “orbitals” are drawn separately. For three conformers (parts a–c in Figure 2) and for **3** (Figure 3), the β spinator bears 90% d character.