Oxo and Hydroxo Bridged Fe(III) Bisporphyrins

The chemistry of cofacial bisporphyrins is currently a topic of great interest, particularly because of their numerous applications in catalysis and their photophysical properties. The most successful cofacial bisporphyrin systems studied to date appear to be related to the so-called “Pac-Man” porphyrin system and have drawn considerable interest due to their small-molecule reactivity. We now provide the first direct support for this crucial conformational change in a single molecular framework which demonstrates the unprecedented ability to open and close its binding pocket forming bisiron(III)μ-oxo dimers. Upon protonation, a novel series of μ-hydroxo species are generated in which two iron centers becomes inequivalent and have different spin states that also varied with the counter anions. This talk will summarize some of our recent results.

Effect of Heme-Heme Interactions: Large Ring Distortion

Inorg. Chem. 2010, 49, 3449
Inorg. Chem. 2008, 47, 10196
Effect of Heme-Heme Interactions: Change in Reactivity

\[ \text{hv} (\lambda > 365 \text{ nm}) \]

Catalytic cycle

- No chemical oxidants
- Only \( \text{O}_2 \) and light

*Inorg. Chem.* 2010, 49, 3449
*Inorg. Chem.* 2008, 47, 10196

Stabilization of Two Different Fe Spins

Counter anion is,

- Very far from the metal ion
- Still controls the iron spins

*Dalton Trans.* 2017, 46, 1012. (Invited Perspective article)
Stabilization of Two Different Fe Spins: Effect of Heme-Heme Interaction

Smallest known Fe-O(H)-Fe angle!

<table>
<thead>
<tr>
<th></th>
<th>Core-I</th>
<th>Core-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O[A]</td>
<td>1.887(3)</td>
<td>1.934(3)</td>
</tr>
<tr>
<td>Fe-N[A]</td>
<td>2.051(3)</td>
<td>2.007(3)</td>
</tr>
<tr>
<td>Fe-O-Fe [Å]</td>
<td>142.5(2)</td>
<td></td>
</tr>
<tr>
<td>A24Fe [Å]</td>
<td>0.55</td>
<td>0.48</td>
</tr>
<tr>
<td>A24 [Å]</td>
<td>0.21</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Spin state  \( S = \frac{5}{2}, \frac{3}{2} \)

Two different spin states in a single molecule for the first time!

\[ \text{J. Am. Chem. Soc. (Communication) 2010, 132, 17983.} \]

\( ^1H \) NMR Spectrum in CDCl\(_3\) at 289K

S: \( \frac{5}{2}, \frac{3}{2} \) in solution
$^1$H NMR spectrum in CDCl$_3$ at 289K

S: 3/2, 3/2 in solution

X-ray Structure

Mossbauer Spectra at 298K

X-ray Structural Parameters at 100K:

<table>
<thead>
<tr>
<th></th>
<th>Core-I</th>
<th>Core-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O [Å]</td>
<td>1.926(3)</td>
<td>1.968(3)</td>
</tr>
<tr>
<td>Fe-N$_5$ [Å]</td>
<td>2.019(4)</td>
<td>1.967(3)</td>
</tr>
<tr>
<td>Fe-O-Fe [°]</td>
<td>148.46(16)</td>
<td></td>
</tr>
<tr>
<td>A24$_b$ [Å]</td>
<td>0.41</td>
<td>0.39</td>
</tr>
<tr>
<td>A24 [Å]</td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>Spin States</td>
<td>3/2, 3/2</td>
<td></td>
</tr>
</tbody>
</table>
$^1$H NMR spectrum in CDCl$_3$ at 292K

S: 3/2, 3/2 in solution

1H NMR Spectrum at 289K

S: 3/2, 3/2 in solution

IS: 0.25 mm/s ; QS: 2.99 mm/s
IS: 0.22 mm/s ; QS: 2.09 mm/s
X-ray Structure

Mosshauer Spectra at 298K

<table>
<thead>
<tr>
<th>X-ray Structural Parameters at 100K:</th>
<th>Core-I</th>
<th>Core-II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-O(Å)</td>
<td>1.907(3)</td>
<td>1.921(3)</td>
</tr>
<tr>
<td>Fe-N₁(Å)</td>
<td>2.062</td>
<td>2.055</td>
</tr>
<tr>
<td>Fe-O-Fe [°]</td>
<td>141.6(2)</td>
<td></td>
</tr>
<tr>
<td>A24Fe(Å)</td>
<td>0.57</td>
<td>0.48</td>
</tr>
<tr>
<td>A24(Å)</td>
<td>0.17</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Spin States: 5/2, 5/2

Stabilization of Two Different Fe Spins: Effect of Heme-Heme Interaction

$^1$H NMR (at 295 K):

\[ X = \text{ClO}_4 \]

\[ X = \text{BF}_4 \]

\[ X = I_3 \]

Variable temperature magnetic study

Counter Anion Specific Spin States

\[ J = -4.5 \text{ cm}^{-1} \]

\[ J = -30 \text{ cm}^{-1} \]

\[ J = -42 \text{ cm}^{-1} \]
Counter Anion Specific Spin States

\[ ^1H \text{NMR} \]

\[ \begin{align*}
\text{X: I}_3 & \quad S = 5/2, 3/2 \\
\text{BF}_4 & \quad S = 5/2(3/2), 3/2(5/2) \\
\text{PF}_6 & \quad -J, \text{ cm}^{-1} = 2.4 \\
\text{SbF}_6 & \quad (3/2, 3/2(5/2) \\
\text{ClO}_4 & \quad 5/2, 5/2 \\
\text{m} \quad & \quad \text{m'} \\
\text{m} \quad & \quad \text{m'}
\end{align*} \]

\[ \text{Variable temperature magnetic study} \]

\[ J = -2.5 \text{ cm}^{-1} \]

\[ J = -36 \text{ cm}^{-1} \]

\[ J = -41 \text{ cm}^{-1} \]


What Role Do Counter Ions Play?
Using Picric Acid for Protonation

UV-vis spectral change

\[
\text{Absorbance} \quad \frac{\text{Wavelength (nm)}}{300 \text{ to } 700}
\]

(A) \[\varepsilon (\text{M}^{-1} \text{cm}^{-1}) \quad \frac{\text{Wavelength (nm)}}{300 \text{ to } 700}\]

(B) \[\text{Absorbance} \quad \frac{\text{Wavelength (nm)}}{300 \text{ to } 700}\]

(C) \[\text{Absorbance} \quad \frac{\text{Wavelength (nm)}}{300 \text{ to } 700}\]

\[\text{high-spin (S=5/2) state}\]


\[^{1}H \text{ NMR in CDCl}_3 \text{ at 295 K}\]

\[\begin{array}{c}
\text{m}''_H \quad \text{m}''_H \quad \text{m}''_m \\
\text{m}''_m \quad \text{m}''_m \quad \text{m}''_m \\
\text{m}''_m \quad \text{m}''_m \quad \text{m}''_m
\end{array}\]

S = 5/2

S = 3/2

S = 5/2

\[\delta, \text{ ppm} \quad \frac{100 \text{ to } 80}{0 \text{ to } -20 \text{ to } -40}\]
**1H NMR Titration in CDCl₃ at 295 K**

![NMR spectrum with chemical shifts and peaks labeled](image)

**Possible Arrangements of the Counter Anion in Solution**

(A) ![Counter anion arrangement 1](image)

(B) ![Counter anion arrangement 2](image)

(C) ![Counter anion arrangement 3](image)

**1H NMR**

![NMR spectrum with chemical shifts and peaks labeled](image)
Spin Flip between Solid and Solution

Formation of μ-fluoro Species

\[^1\text{H NMR}\]

S: 3/2, 3/2

Iron centers are equivalent

Iron centers are non-equivalent

$^1$H NMR: Comparison between Fe(III) and Mn(III) Complexes

Mn$^{III}$Mn: 3.752(1)

Fe$^{III}$Fe: 3.627(1)

Inter-ring interactions

core I ≠ core II

core I ≠ core II

core I = core II

core I = core II

Inter-porphyrin distance

Inorg. Chem. 2016, 55, 3239
Representative Publications:

1. **Oxo- and Hydroxo-bridged Diiron(III) Porphyrin Dimers: Inorganic and Bio-inorganic Perspectives and Effects of Intermacroyclic Interactions**

   T. Guchhait, S. Sasmal, F. S. T. Khan, and S. P. Rath*


2. **Hydroxo-Bridged Diiron(III) and Dimanganese(III) Bisporphyrins: Modulation of Metal Spins by Counter Anions**

   F. S. T. Khan, T. Guchhait, S. Sasmal and S. P. Rath*

   *Dalton Trans. 2017, 46, 1012-1037 (Invited Perspective and Cover page Article)*
3. **Remarkable Anion Dependent Spin state Switching in Diiron(III)-µ-Hydroxo Bisporphyrins: What role do Counter ions play?**

   F. S. T. Khan and S. P. Rath*


4. **Diiron(III)-µ-fluoro Bisporphyrins: Effect of Bridging Ligand on the Metal Spin State**

   D. Sil, A. Kumar and S. P. Rath


5. **Effect of Inter-porphyrin Distance on Spin-state in Diiron(III) µ-Hydroxo Bisporphyrins**

   D. Sil and S. P. Rath*


6. **Experimental and Theoretical Investigation on a Series of Novel Dimanganese(III)-µ-hydroxo Bisporphyrins: Magneto-Structural Correlation and Effect of Metal Spin on Porphyrin Core Deformation**

   D. Sil, S. Bhowmik, F. Khan and S. P. Rath*


7. **Spin State Ordering in Hydroxo Bridged Diiron(III)bisporphyrin Complexes**

   M. A. Sainna, D. Sil, D. Sahoo, B. Martin, S. P. Rath,* P. Comba* and S. P. de Visser*


8. **Ethane-bridged Porphyrin Dimer as Model of Di-heme Proteins: Inorganic and Bioinorganic Perspectives and Consequences of Heme-Heme Interactions**

   D. Sil and S. P. Rath*

   *Dalton Trans. 2015, 44, 16195 - 16211. (Invited Perspective Article)*


   S. Bhowmik, S. Dey, D. Sahoo and S. P. Rath*
Effect of Heme-Heme Interactions and Modulation of Metal Spins by Counter Anions in a Series of Diiron(III)-µ-hydroxo Bisporphyrins: Unusual Stabilization of Two Different Spins in a Single Molecular Framework

S. K. Ghosh, S. Bhowmik, D. Sil and S. P. Rath*


Protonation of an oxo-Bridged Diiron Unit Makes Two Iron Centers Different: A New Class of Diiron(III)-µ-hydroxo Bisporphyrin and Control of Spins by Counter Anions

S. Bhowmik, S. K. Ghosh, S. Layek, H. C. Verma and S. P. Rath*


Control of Spins by Ring Deformation in a Diiron(III)bisporphyrin: Reversal of ClO₄⁻ and CF₃SO₃⁻ Ligand Field Strength on the Magnetochemical Series

S. Bhowmik, S. K. Ghosh and S. P. Rath*


S. K. Ghosh and S. P. Rath*


Synthesis and Characterization of Anti-bisFe(III) Porphyrins, Syn-bisFe(III)-µ-oxo Porphyrin and Syn-bisFe(III)-µ-oxo Porphyrin Cation Radical

S. K. Ghosh, R. Patra and S. P. Rath*


Remarkably Bent, Ethane-Linked, Diiron(III) µ-Oxobisporphyrin: Synthesis, Structure, Conformational Switching, and Photocatalytic Oxidation

S. K. Ghosh, R. Patra and S. P. Rath*