Oxo and hydroxo bridged diiron active centers are common structural motifs found in a variety of proteins in biology. The highly versatile oxo/hydroxo-bridged dimetallic centers, regulated by a simple protonation/deprotonation process, permits the enzyme a natural way to control the intermediates in the catalytic cycles. The chemical and electrochemical nature of the Fe-O-Fe/Fe-O(H)-Fe unit are suitably controlled by the inter-macroyclic interaction between two heme centers and thereby influence the structure, property and reactivity of the molecule to a large extent. A close approach of the two rings in the ethene and ethane-bridged μ-hydroxo complex results in an unequal core deformations that leads to unusual stabilization of two different spin states of iron(III) in a single molecular framework. Also, spin states vary on the counter ion (X) used and are reversibly interconvertible although the counter anions are far away and not apparently involved in any kind of direct interactions with the metal ion. The small environmental perturbations coming out of the counter anion, H-bonding interaction, heme-heme interaction etc. can change the structure and properties of the individual heme centers drastically and it seems very likely that Nature uses some of these techniques to control the property of the biomolecules for a specific function.
Effect of Heme-Heme Interactions: Large Ring Distortion

Smallest known Fe-O-Fe angle!

Effect of Heme-Heme Interactions: Change in Reactivity

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

- No chemical oxidants
- Only \( O_2 \) and light

*Time evaluation spectra: Reaction with P(OEt)_3 under anaerobic condition*
Stabilization of Two Different Fe Spins

Counter anion is,
- Very far from the metal ion
- Still controls the iron spins

Two different spins of Fe in a single molecule!!

*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 [Å]</td>
<td>1.887(3)</td>
<td>1.934(3)</td>
</tr>
<tr>
<td>Fe-N$_{Fe}$ [Å]</td>
<td>2.051(3)</td>
<td>2.007(3)</td>
</tr>
<tr>
<td>Fe-O-Fe [Å]</td>
<td>142.5(2)</td>
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</tr>
<tr>
<td>A$_{24}^{Fe}$ [Å]</td>
<td>0.55</td>
<td>0.48</td>
</tr>
<tr>
<td>A$_{24}$ [Å]</td>
<td>0.21</td>
<td>0.38</td>
</tr>
<tr>
<td>Spin state</td>
<td>$S = 5/2, 3/2$</td>
<td></td>
</tr>
</tbody>
</table>

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


$^1$H NMR Spectrum in CDCl$_3$ at 289K

S: 5/2, 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$_{Fe}$ [Å]</td>
<td>2.619(4)</td>
<td>1.967(3)</td>
</tr>
<tr>
<td>Fe-O-Fe $^{[\sigma]}$</td>
<td>148.46(16)</td>
<td></td>
</tr>
<tr>
<td>A24$^{[\sigma]}$ [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>
</tbody>
</table>

Spin States: 3/2, 3/2
**$^1$H NMR spectrum in CDCl$_3$ at 292K**

![NMR spectrum diagram]

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

**$^1$H NMR Spectrum at 289K**

![NMR spectrum diagram]

S: 3/2, 3/2 in solution

$-\text{CH}_3$
**X-ray Structure**

![X-ray structure diagram](image)

**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>1.907(3)</td>
<td>1.921(3)</td>
</tr>
<tr>
<td>Fe-N₄[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>A24[^#]</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**

![Stabilization diagram](image)

**4H NMR (at 295 K):**

- For X=ClO₄:
  - m, m'
  - -CH₂⁻

- For X=BF₄:
  - m, m'
  - -CH₂⁻

- For X=I₃:
  - m, m'
  - -CH₂⁻

**Variable temperature magnetic study**

![Magnetic study graph](image)

**Counter Anion Specific Spin States**

Counter Anion Specific Spin States

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

![UV-vis Spectral Change Diagram]

high-spin (S=5/2) state


$^1$H NMR in CDCl$_3$ at 295 K

![NMR Spectra Diagram]
$^1$H NMR Titration in CDCl$_3$ at 295 K

Possible Arrangements of the Counter Anion in Solution

(A) $^1$H NMR

(B) $^1$H NMR

(C) $^1$H NMR
Spin Flip between Solid and Solution

Formation of μ-fluoro Species

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 $\neq$ core II  
core I $\neq$ 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*


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


11. **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*


12. **Control of Spins by Ring Deformation in a Diiron(III)bisporphyrin: Reversal of ClO$_4^-$ and CF$_3$SO$_3^-$ Ligand Field Strength on the Magnetochemical Series**

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

*Chem. Commun. 2011, 47, 4790 - 4792.*


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


14. **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*


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