5.111 Principles of Chemical Science
Fall 2008

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Metals in Biology: Crystal Field Theory and Magnetism  
*See lectures 28 and 29 for an introduction to crystal field theory.*

**Magnetism**
Compounds possessing unpaired electrons are **paramagnetic** (attracted by magnetic field); those in which the electrons are paired are **diamagnetic** (repelled by magnetic field).

**Example from page 4 of Lecture 29 notes: Inspiration from Metalloenzymes for the Reduction of Greenhouse Gasses.**

Researchers are very interested in developing new catalysts for removing harmful greenhouse gasses, such as carbon monoxide (CO) and carbon dioxide (CO$_2$) from the atmosphere.

Nature has already figured out how to accomplish this. Certain microbes “live on” CO or CO$_2$, utilizing enzymes with metal cofactors that facilitate carbon fixation reactions.

Microbes remove ~100 million tons of CO from atmosphere each year and produce ~1 trillion kg of acetate annually from greenhouse gases.

**Bacteria that live on greenhouse gasses**

<table>
<thead>
<tr>
<th><em>Carboxydothermus hydrogenoformans</em></th>
<th><em>Moorella thermoacetica</em></th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
</tr>
<tr>
<td>$\text{H}_2\text{O} + \text{CO} \rightarrow \text{H}_2 + \text{CO}_2$</td>
<td>$4 \text{H}_2 + 2 \text{CO}_2 \rightarrow \text{CH}_3\text{COOH} + 2 \text{H}_2\text{O}$</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>$2 \text{H}_2\text{O} + 4 \text{CO} \rightarrow \text{CH}_3\text{COOH} + 2 \text{CO}_2$</td>
<td>$\text{H}_2\text{O} + \text{CO} \rightarrow \text{CH}_3\text{COOH} + 2 \text{CO}_2$</td>
</tr>
</tbody>
</table>

- Highly active CO metabolism  
- Strict anaerobe  
- Doubling time on CO is 2 hours  
- Optimum temperature: 70 °C.

- Model acetogenic bacterium  
- Strict anaerobe  
- Optimum temperature: 55 °C.

How are these reactions facilitated? **Metal clusters in enzymes.**

Nickel is key to this amazing chemistry, but in order to mimic Nature’s solution, it is essential to know the geometry around the Ni center.
Putting it all together: If a Ni$^{2+}$ (d$^8$) center in an enzyme is found to be diamagnetic, does it have square planar, tetrahedral, or octahedral geometry?

\[
\begin{align*}
E & \quad \underline{d_{x^2-y^2}} \\
& \quad \underline{d_{x^2}} \quad \underline{d_{y^2}} \\
& \quad \underline{d_{xy}} \quad \underline{d_{xz}} \quad \underline{d_{yz}} \\
& \quad \underline{d_{x^2-y^2}} \quad \underline{d_{x^2}} \\
\text{(Octahedral crystal field)} & \quad \underline{d_{xz}} \quad \underline{d_{yz}} \\
\text{(Square planar crystal field)} & \quad \underline{d_{x^2-y^2}} \quad \underline{d_{x^2}} \\
\text{(Tetrahedral crystal field)}
\end{align*}
\]

**Answer:**
The Ni site has a square planar geometry.
(Fill in the 8 d-electrons in each diagram to see that only the square planar field will result in no unpaired electrons.)

This square planar Ni site is found in an enzyme called acetyl-CoA synthase, which catalyzes reactions that consume CO$_2$ and CO.

square planar Ni