5.111 Principles of Chemical Science
Fall 2008

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

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

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

Photo courtesy of Dr. Edwin P. Ewing.

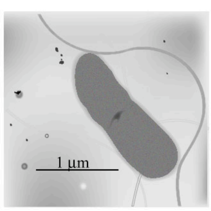
Researchers are very interested in developing new catalysts for removing harmful greenhouse gasses, such as carbon monoxide (CO) and carbon dioxide (CO_2) from the atmosphere.

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

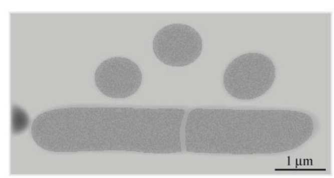
Carboxydothermus hydrogenoformans



$H_2O + CO \rightarrow H_2 + CO_2$

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

Moorella thermoacetica

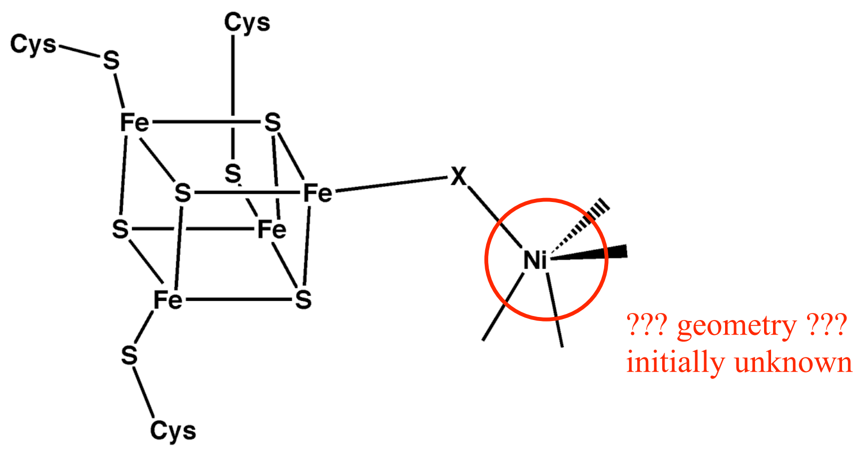


$4\ H_2 + 2\ CO_2 \rightarrow CH_3COOH + 2\ H_2O$
$2\ H_2O + 4\ CO \rightarrow CH_3COOH + 2\ CO_2$

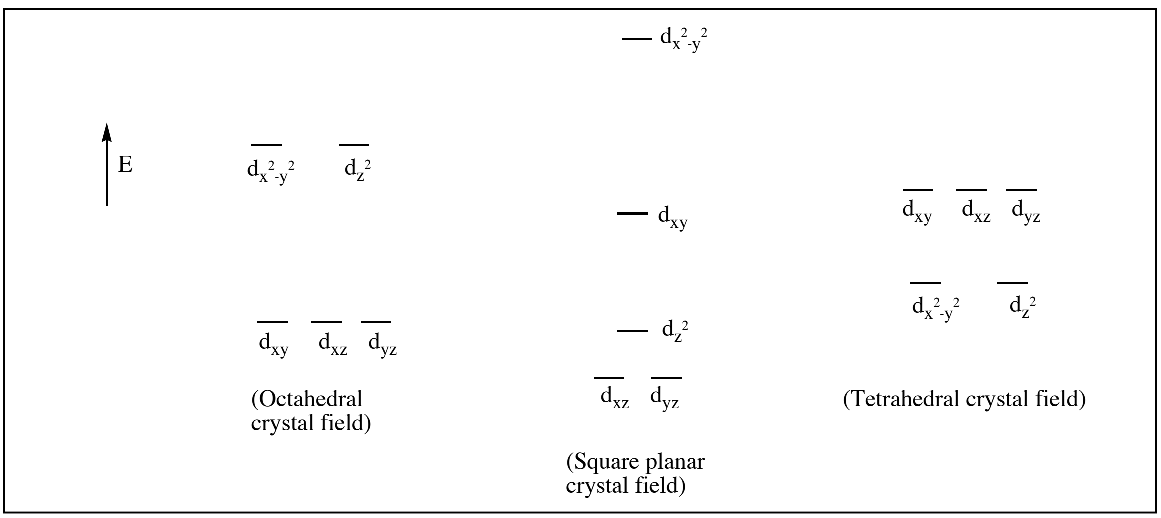
- Model acetogenic bacterium
- Strict anaerobe
- Optimum temperature: 55 °C.

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.



<u>Putting it all together</u>: If a Ni^{2+} (d^8) center in an enzyme is found to be diamagnetic, does it have square planar, tetrahedral, or octahedral geometry?



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.