

Chem 1B Objective 16:

Understand coordinate covalent bond and structure of coordination compounds.

Key Ideas:

Chem 1A: metal and non-metal form an ionic compound (ionic bond).

Some metals form covalent bond to a non-metal, usually to C or N. This bond is a *coordinate covalent* bond (2 electrons from non-metal combines with metal). Compare to covalent bond (1 unpaired electron from one atom combines with 1 unpaired electron from another atom).

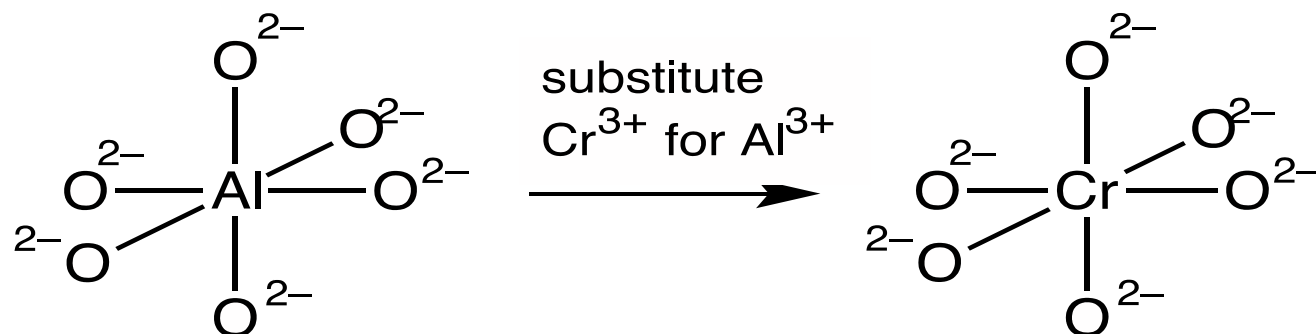
Chem 1A: octet rule

Coordination compounds have an expanded octet – more than 8 electrons around central atom (usually metal).

Most **Main Group** Compounds Are **White**
Most **Transition Metal** Compounds Are **Colored**

Color of gemstones (<http://www.scifun.org/chemweek/Gemstones/Gemstones.html>)

Rubies are red. Why?



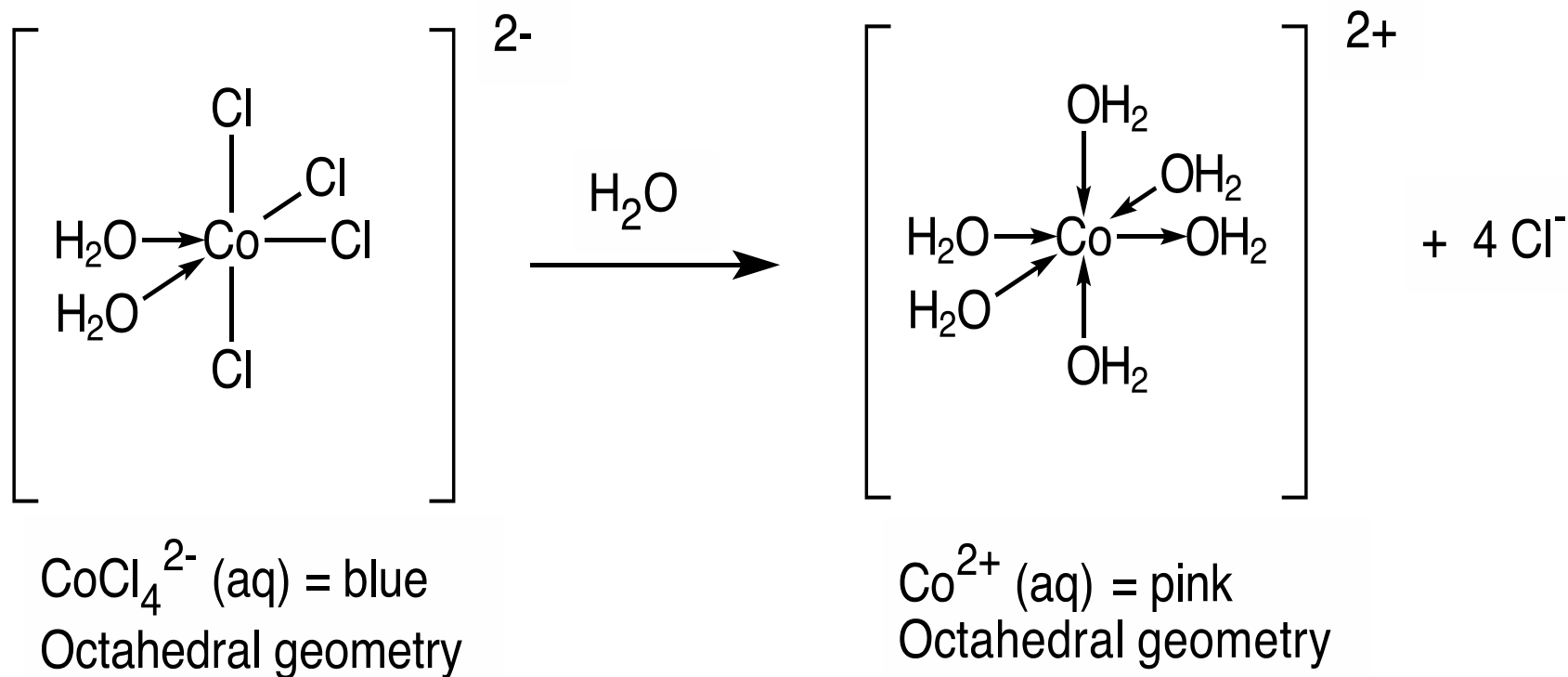
Alumina: Al^{3+}
surrounded by 6 O^{2-}
Colorless
Octahedral geometry

Ruby: Cr^{3+}
surrounded by 6 O^{2-}
Red
Octahedral geometry

[http://
www.mnh
.si.edu/
exhibits/
ruby/](http://www.mnh.si.edu/exhibits/ruby/)

Change metal ---> change **color**

Drierite - color indicator in drying agents (see Lab 4)
Blue means dry; **Pink** means wet

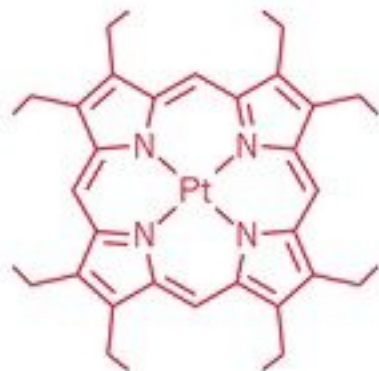


Write an equilibrium equation that represents this reaction.

Change substance bonded to Co^{2+} --> change **color**

OLEDs need colored compounds

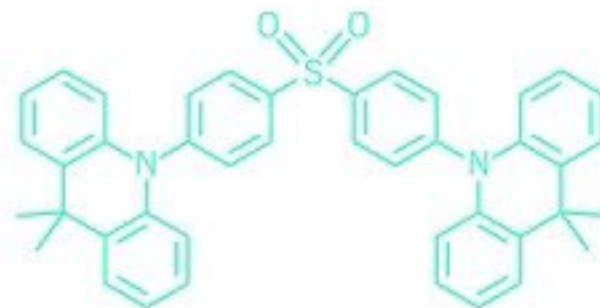
<http://cen.acs.org/articles/94/i28/rise-OLED-displays.html>



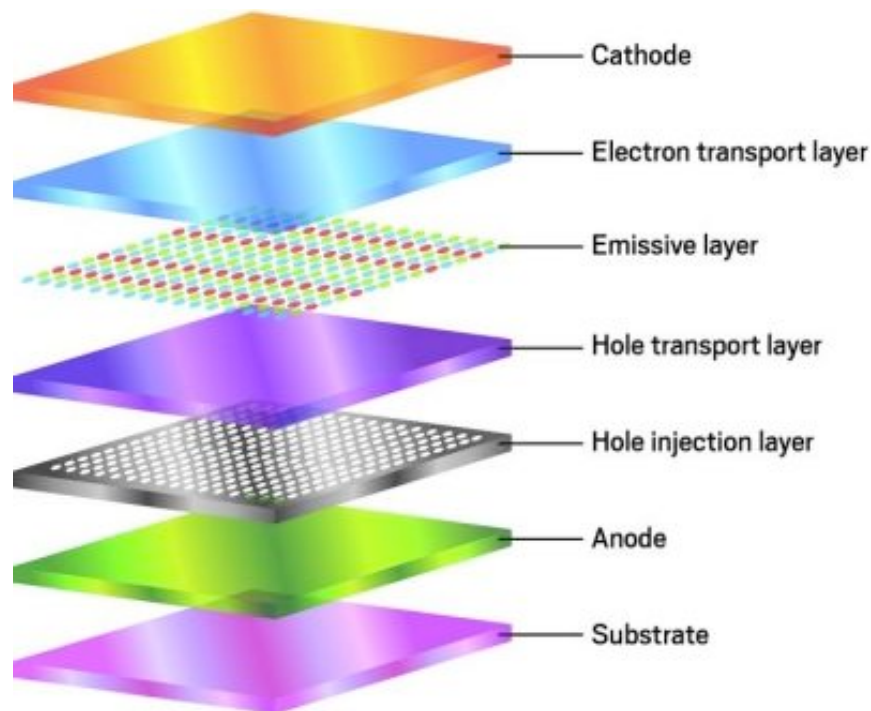
Platinum octaethylporphyrin



Tris[2-phenylpyridinato-C²,N]iridium(III)



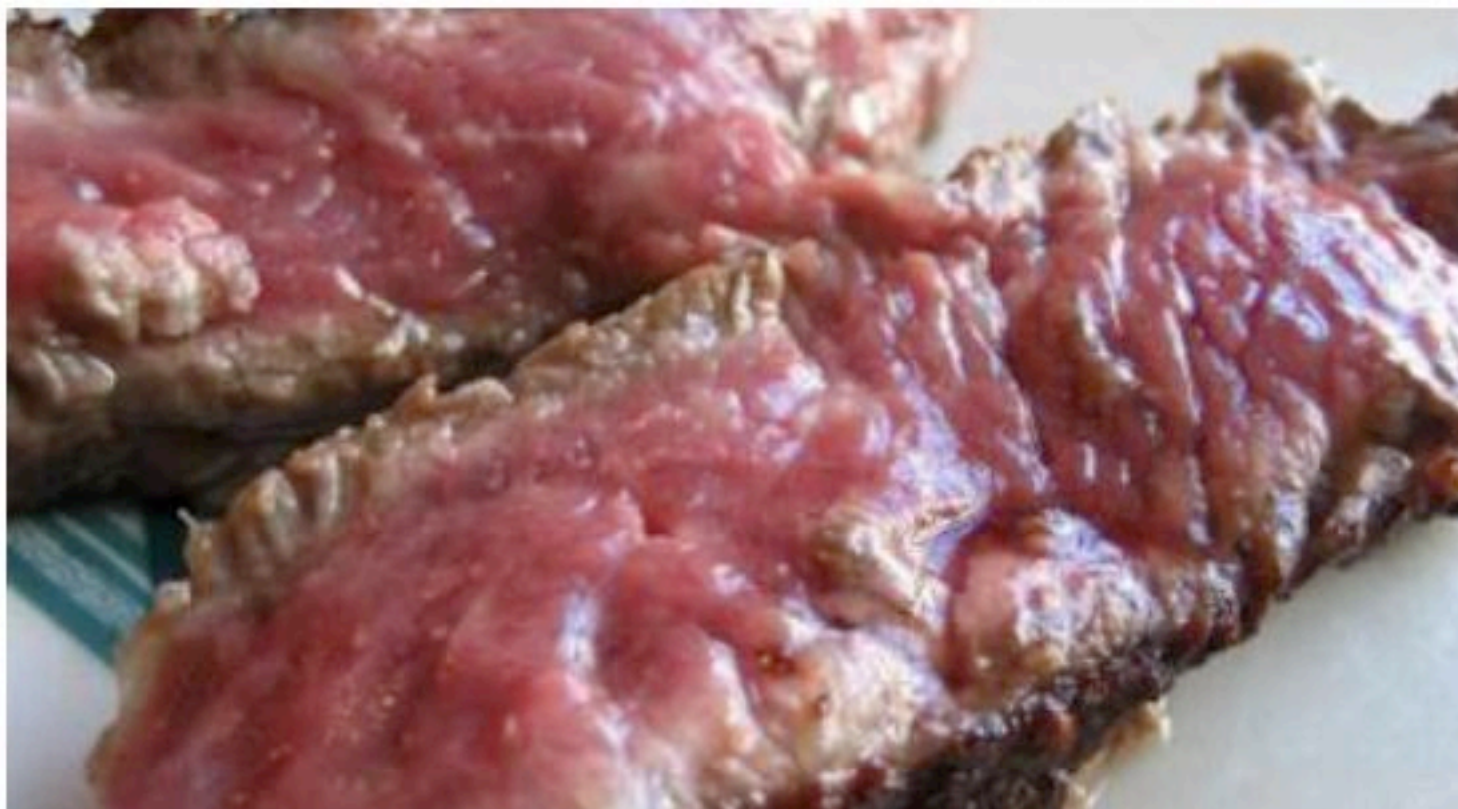
Diphenylsulfone dimethyldihydroacridine



How OLEDs work

An OLED can be manufactured using a variety of substrates, including glass, plastic, and metal. It consists of several layers of organic materials sandwiched between two electrodes. When a voltage is applied across the OLED, a current of electrons flows from the cathode to the anode, adding electrons to the emissive layer and taking them away—or creating electron holes—at the anode. At the boundary between these layers, electrons find holes, fall in, and give up a photon of light. The color of the light depends on the type of organic molecule in the emissive layer. The most advanced OLEDs use electron and hole injection and transport layers to modulate electron movement.

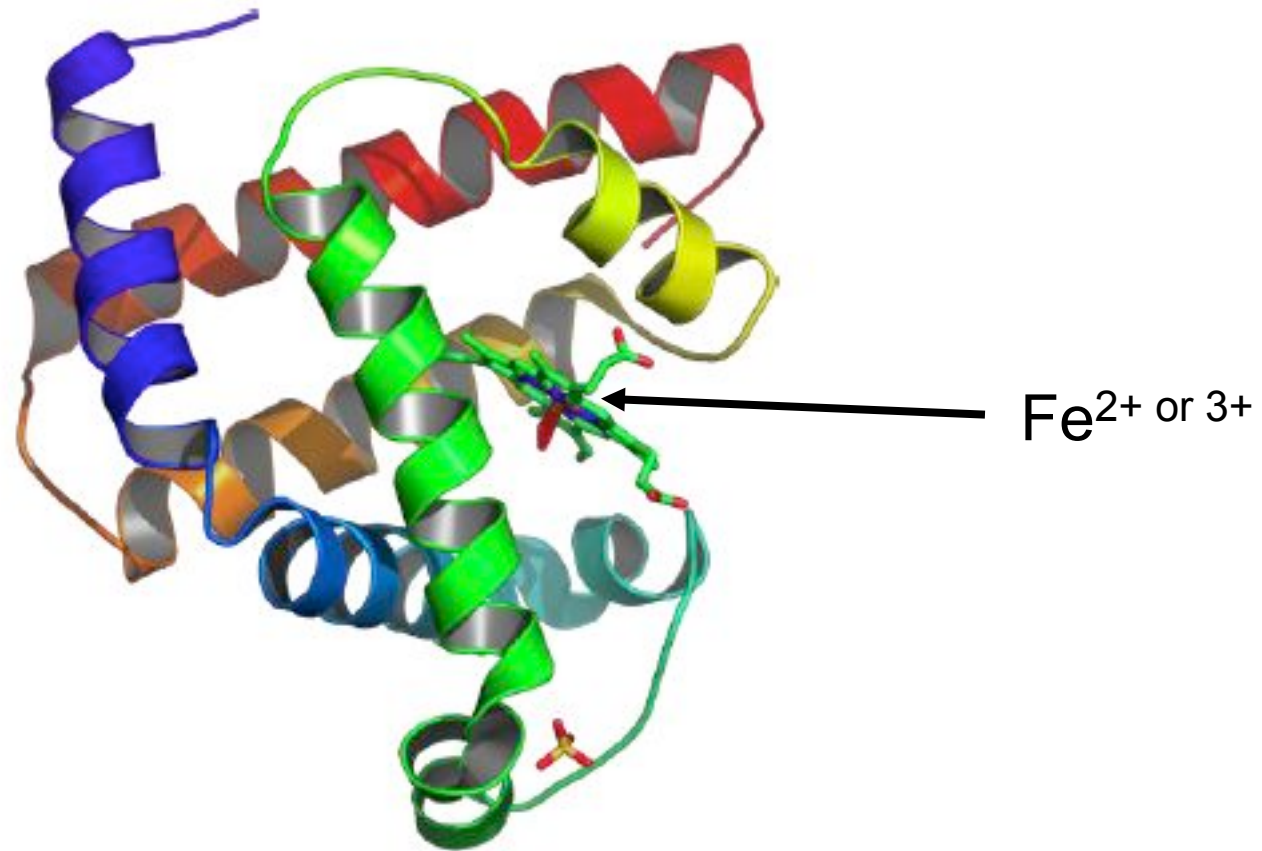
Meat color and Chemistry



The **Color of Meat** depends on the Substance that
Binds to **Myoglobin**

ACS Webinar: Advanced Culinary Chemistry: The Science of the Grill (6/30/11)

Myoglobin Is an Oxygen Binding Protein Found in Muscle



The substance, e.g., H_2O or O_2 , that binds to Fe determines the **color** of myoglobin

The ***Color of Meat*** depends on the Substance that Binds to ***Myoglobin***
Which Piece of Meat Would You Buy?



Deoxymyoglobin
Purple red
 Fe^{2+}

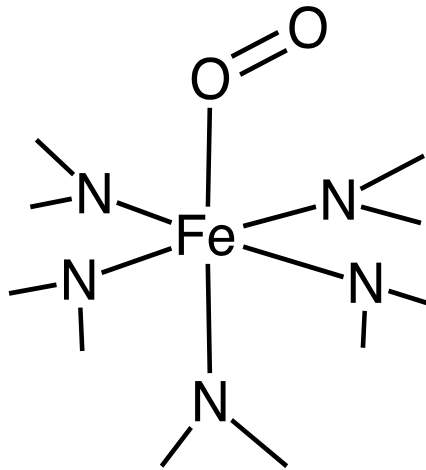


Oxymyoglobin
Red
 O_2 binds to Fe^{2+}

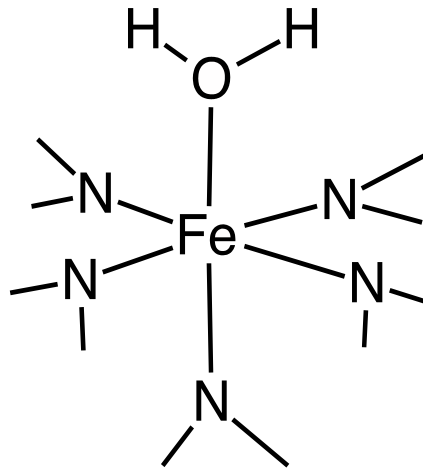


Metmyoglobin
Brown
 H_2O binds to Fe^{3+}

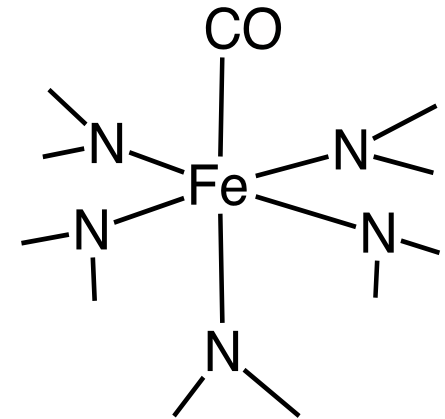
The **Color of Meat** depends on the Substance that
Binds to **Myoglobin**



Oxymyoglobin
 Fe^{2+}
red



Metmyoglobin
 Fe^{3+}
brown



Carboxymyoglobin
 Fe^{2+}
red

Change charge on Fe --> change **color**

Change substance bonded to Fe --> change **color**

Which Piece of Meat Would You Buy?

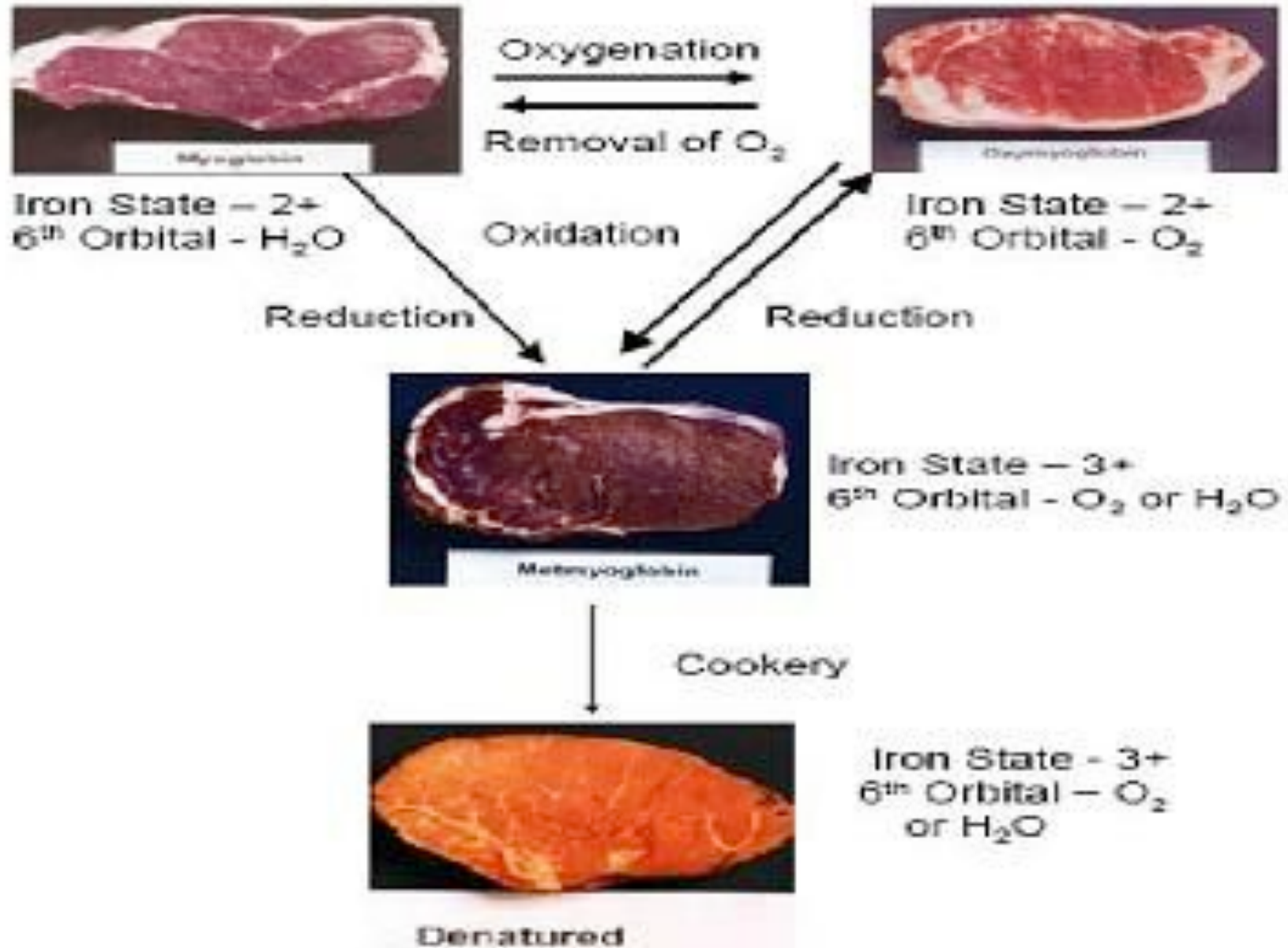


Each piece is a **1 week old** sirloin

Left: carboxymyoglobin

Right: metmyoglobin

Fresh Meat Color Reactions



<http://meatcolour.wikispaces.com/>

Would You Eat a Pink Pork?

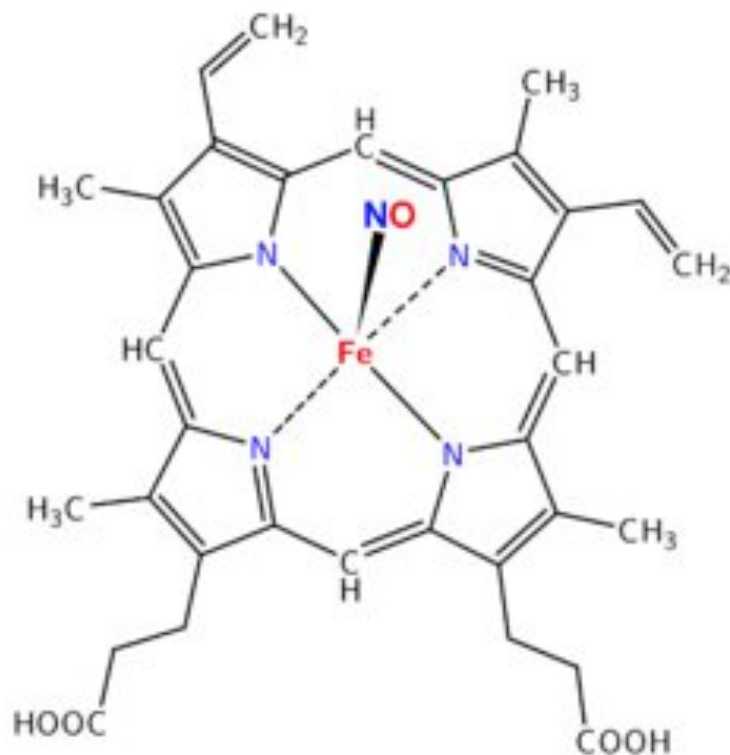
Nitrosohemochrome & “Smoke Ring”



Nitrogen dioxide (NO_2 , leading to nitric acid and nitrosohemochrome); promoted by high nitrogen content in fuel; similar to curing with nitrites

In meat: Nitrite (NO_2^-) \rightarrow nitric oxide (NO)

NO_2^- inhibits botulism (bacteria) growth



<http://ourbestbites.com/2010/04/quick-tip-cooking-bacon/>

Nitrosohemochrome (nitrosyl heme) – **pink** color

See ham, cured meats (bacon, hot dogs, sausage)

[https://en.wikipedia.org/wiki/Curing_\(food_preservation\)](https://en.wikipedia.org/wiki/Curing_(food_preservation))

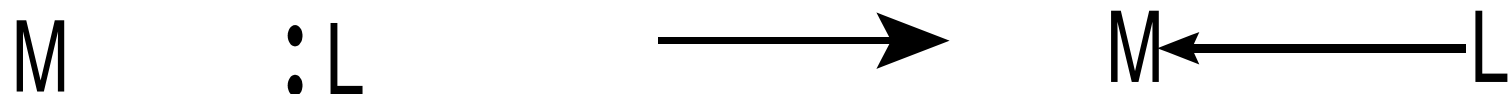
https://en.wikipedia.org/wiki/Sodium_nitrite

<http://www.sciencedaily.com/releases/2002/11/021113070827.htm>

Covalent bond: bonding pair of e⁻ comes from 1 unpaired e⁻ from one atom and 1 unpaired e⁻ from another atom



Coordinate covalent bond: bonding pair of e⁻ comes from **same** atom



M = metal

L = **ligand** (contributes 2 electrons)

Coordination Chemistry Involves A Metal Covalently Bonded to A Non-Metal

Compare organic chemistry to coordination chemistry:

Organic Chemistry	Coordination Chemistry
Carbon	Transition metals
Period 2	Periods 4, 5, 6
2s 2p	(n-1)d (ns np)
4 bonds to carbon	4, 5, 6 bonds to metal
Octet rule = 8 electrons	16 and 18 electron rule
Tetrahedral	Octahedral
Functional groups	Ligands
White compounds	Colored compounds
Covalent bond	Coordinate covalent bond

Transition Metals Can form more than 4 Bonds
TMs Use s, p, and d Orbitals and Can Have An
Expanded Octet: the 18 electron rule and 16 electron rule.

- 1.a. Count the electrons in $\text{Fe}(\text{CO})_5$ and $\text{Cr}(\text{CO})_6$.
 - b. Determine the geometry in each compound. Hint: VSEPR
-
2. Chelates, chelating agent and sequesterants:
 - a. Ethylene diamine and EDTA are used as food preservatives. How do they work?
 - b. Why is Pb and Cd used in paint?

The Color of Transition Metal Compounds is Due to
the Splitting of d Orbitals and the Ligand
See Chang, 6th ed., p. 717, Fig. 20.15 TM ions colors

Coordination Compounds often have a tetrahedral shape or
octahedral shape.

The shape determines the type of d orbital splitting.

Crystal field splitting tutorial

(<http://www.wwnorton.com/college/chemistry/chemistry3/ch/18/chemtours.aspx>)

The Ligand Field Strength how much the d orbitals split

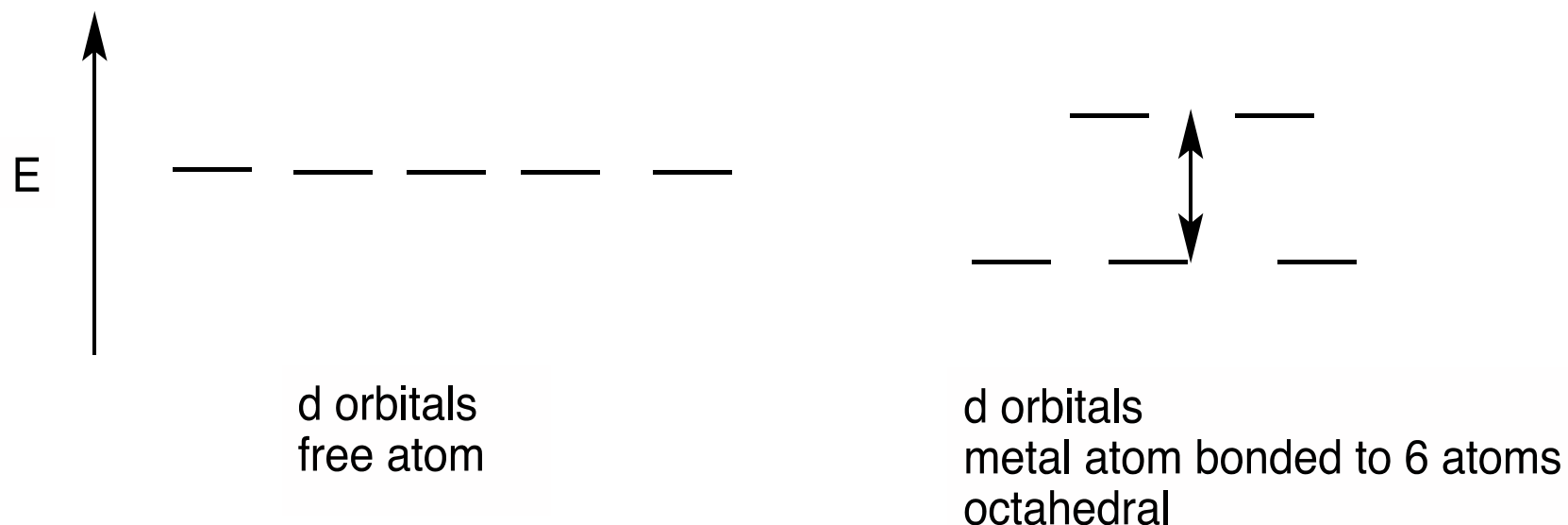
The **Spectrochemical Series** ranks ligand field strength

$I^- < Br^- < Cl^- < OH^- < F^- < H_2O < NH_3 < en < CN^- < CO$

Why is blood red?

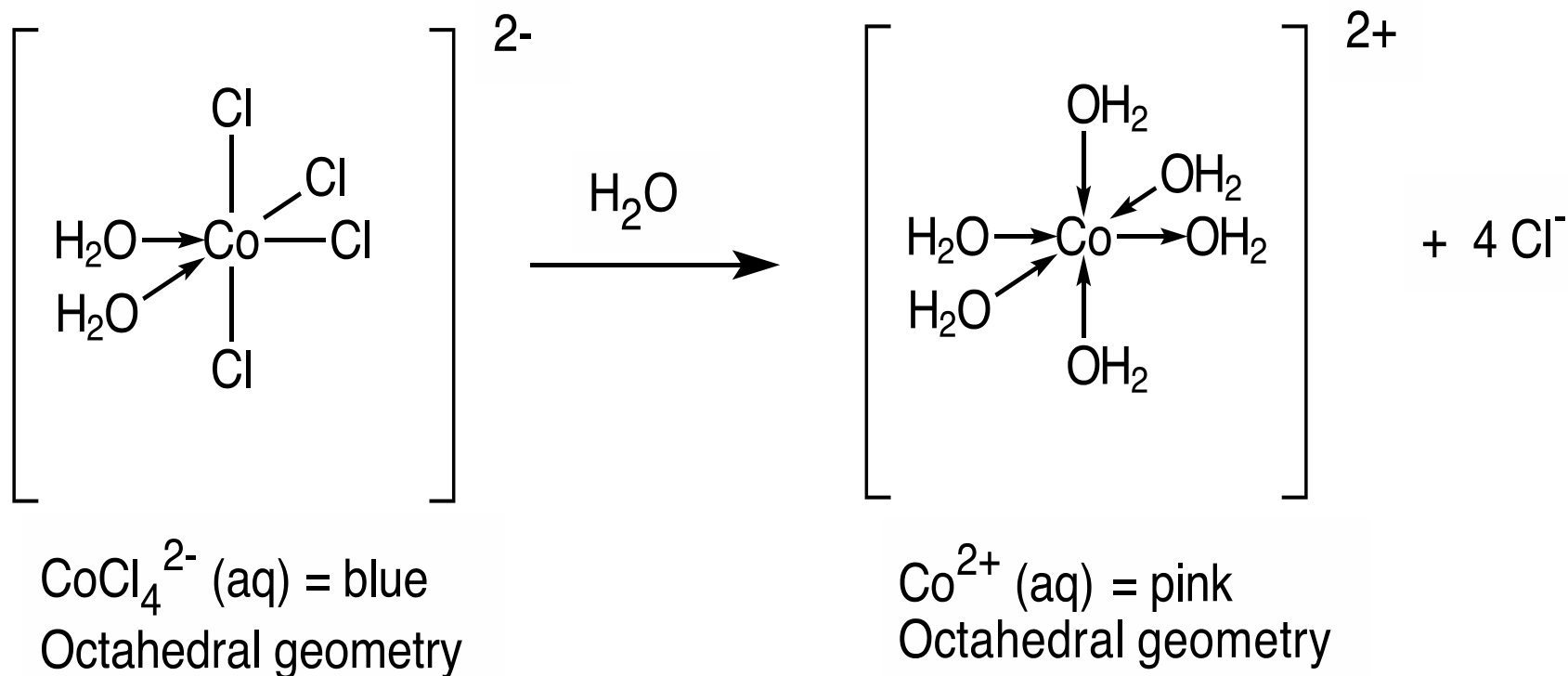
Chang, 6th ed., p. 725, Problem 20.46

Energy Difference (splitting) depends in Ligand bonded to Metal
Strong field ligand --> larger splitting
Weak field ligand --> smaller splitting



*You can design specific **colors** by changing the ligand bonded to a metal.*

Drierite - color indicator in drying agents (see Lab 4)
Blue means dry; **Pink** means wet



Spectrochemical series: Cl^- is a **weaker** field ligand than H_2O
 Complementary color of blue is orange (lower E ==> smaller splitting)
 Complementary color of pink is green (higher E ==> larger splitting)

Metals Are Found In Biology and Medicine

1. What elements are found in the human body?

<http://chemistry.about.com/cs/howthingswork/f/blbodyelements.htm>

CEN, 7/26/10, p. 7 Metals in microbial metalloproteins: V, Mn, Fe, Co, Ni, Zn, Mo, W, Pb, U

2. What are trace elements?

<http://www.healthtree.com/articles/supplements/trace-elements.php>

Bruce Ames: micronutrients (folic acid, Vitamins K and D, Se, ..) prevent disease (CEN, 2/14/11, p. 38)

3. What is the role of metals in the body?

http://wiki.answers.com/Q/What_is_the_role_of_metals_in_human_body

Platinum: cis-platin as cancer drug

Iron is found in Heme Proteins: hemoglobin, cytochrome, catalase and peroxidase, etc.

70 kg human contains about 3.7 g of Fe (70% in hemoglobin, 30% in ferritin).

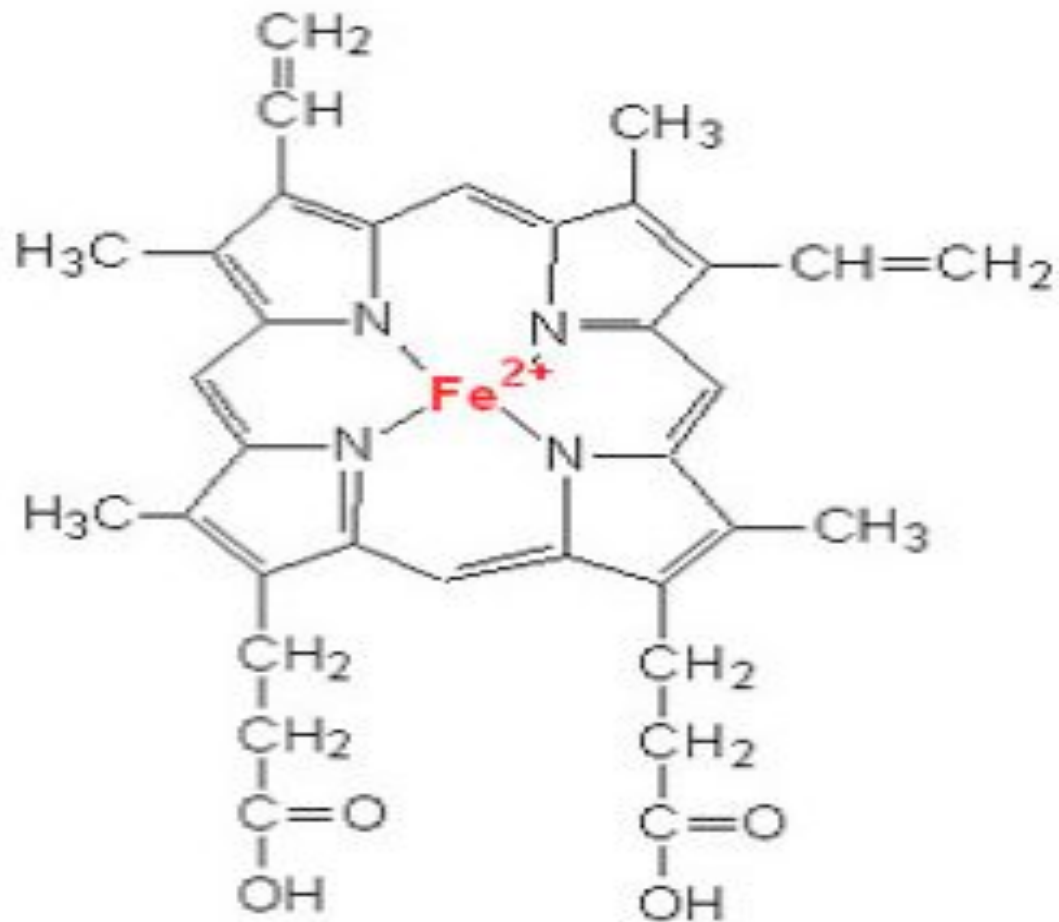
Heme = Fe-protoporphyrin IX, non-polypeptide (not a protein), square planar at Fe. (See structure: <http://en.wikipedia.org/wiki/Heme>)

Many proteins require a tightly bound, specific non-polypeptide units for their biological activity → prosthetic group.

A protein without its characteristic prosthetic group is called an apoprotein.

What is a coenzyme?

Hemoglobin – only ferroheme (Fe²⁺) binds O₂.



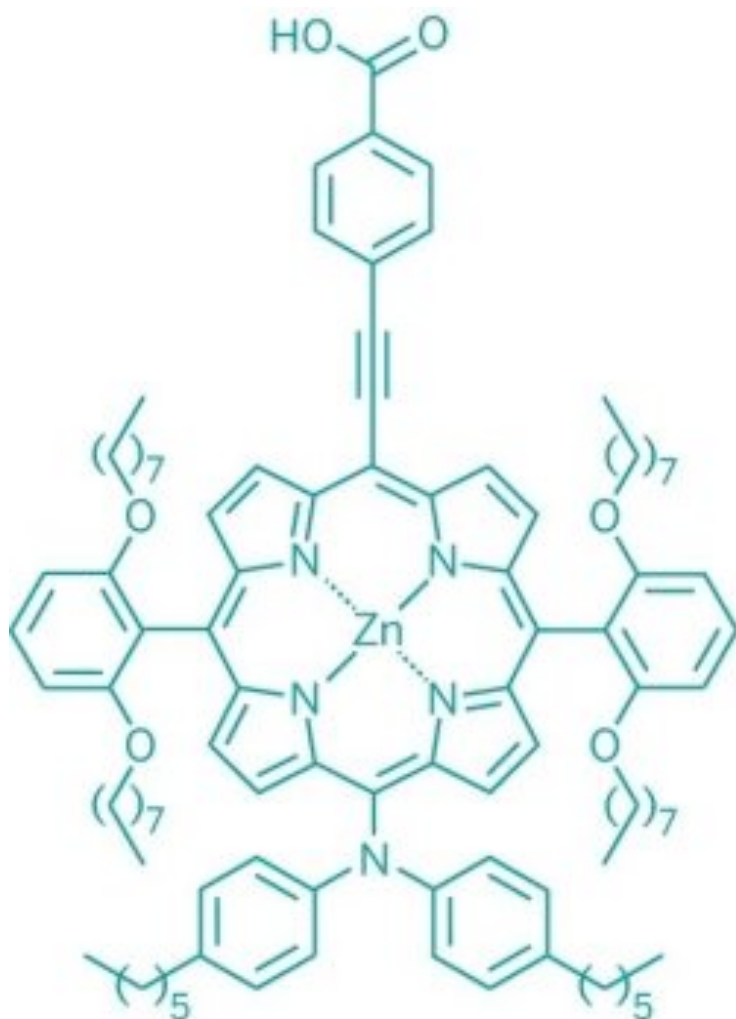
Heme b

Iron protoporphyrin IX

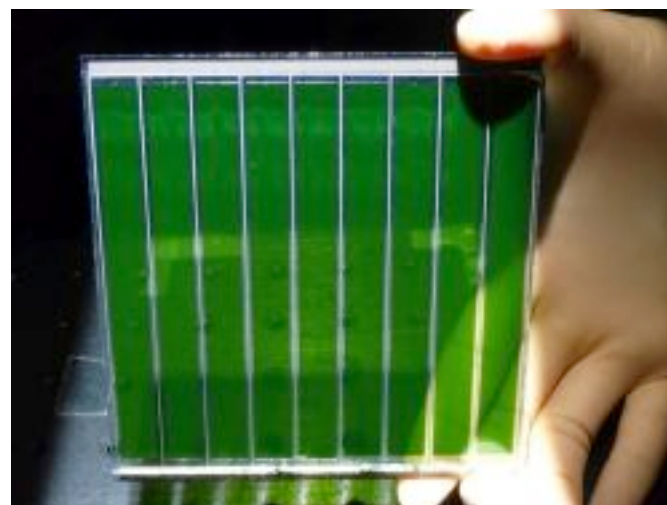
<http://themedicalbiochemistrypage.org/heme-porphyrin.php>

<http://cen.acs.org/articles/89/i45/Better-Dye-Yields-Better-Solar.html>

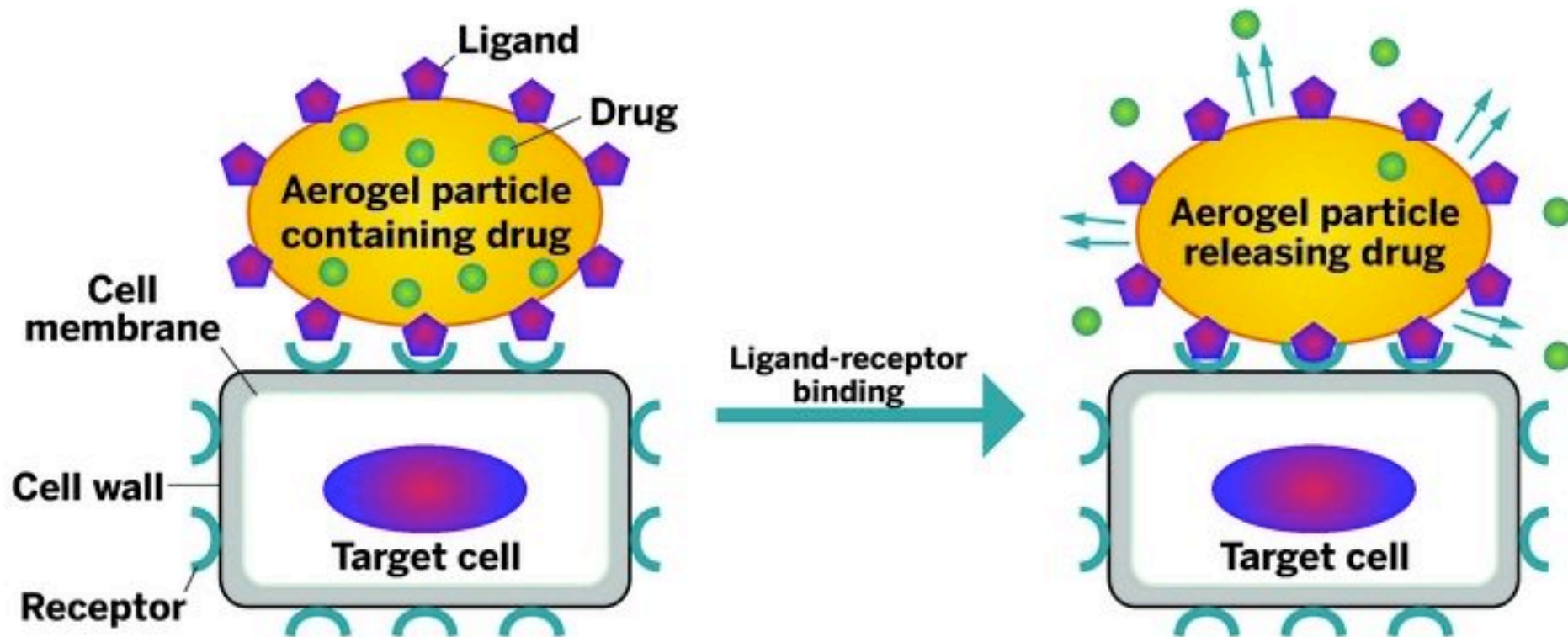
11/7/11, CEN, p. 9 Zn porphyrin dye in dye sensitized solar cell sets record for power conversion efficiency (12.3%)



Customized zinc porphyrin dye



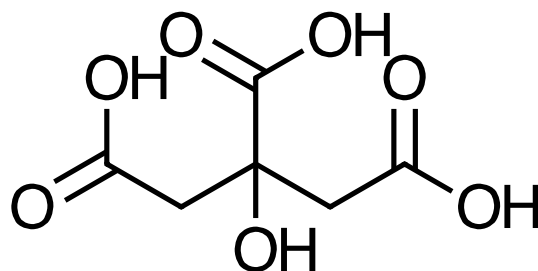
1/27/14, C&EN, p. 29 (<http://cen.acs.org/articles/92/i4/New-Vehicle-Drug-Delivery.html>)
Ligands Help Deliver Drugs to Target Cells



C&EN, 3/7/16, p. 12, Use **Orange** Peels to Remove Copper from Water



Citric acid binds to Cu(II) ions



$$\text{pK}_{\text{a}1} = 3.13$$

$$\text{pK}_{\text{a}2} = 4.76$$

$$\text{pK}_{\text{a}3} = 6.4$$

<http://curiousclarinetist.blogspot.com/2011/02/humidifying-your-case.html>

What must be charge on citric acid for Cu²⁺ to bind to it?

At what pH is this charge on citric acid?

Cyanide in My Table Salt??

<http://cen.acs.org/articles/94/i3/Nonstick-Salt-Electrochemistry-Heroes-Fishy.html>



Salt absorbs H_2O from air (hygroscopic) → dissolves

When the salt dries out, the salt crystals fuse (*cake*) together.

Anticaking agent = Yellow Prussiate of Soda = $\text{Na}_4[\text{Fe}(\text{CN})_6] \cdot 10 \text{H}_2\text{O}$

Cyanide = CN^- ion

Why do you think Yellow Prussiate of Soda is used although it contains *cyanide*?

Other anti-caking agents: calcium silicate, tricalcium phosphate, NaHCO_3 , rice flour.

Review

1. Adding a product shifts an equilibrium reaction:

- a. to the product side
- b. to the reactant side
- c. no change

Key words:

Key equations:

2. _____ tells you whether a reaction occurs spontaneously.

a. ΔH

b. ΔS

c. ΔG

Key words:

Key equations:

3. A battery _____ energy and has a E° _____.

a. supplies

d. greater than 0

b. Produces

e. less than 0

c. Gives

f. equal

Key words:

Key equations:

4. Battery acid contains _____ and _____ and has a _____ pH.

a. H_2SO_4 / SO_4^{2-} / 18 M

b. H^+ / SO_4^{2-} / low

c. H^+ / HSO_4^- / low

Key words:

Key equations:

5. U-234 is an alpha emitter with a _____ of 247,000 years. This _____ reaction is a _____ order with a rate constant of _____.

a. low-life / radioactive / second / 1 sec

b. half-life / radioactive decay / first / 2.8×10^6

c. half-life / nuclear / first / 2.8×10^{-6}

Key words:

Key equations:

6. _____ tells you how fast a reaction occurs; _____ tells you how much products are produced; _____ tells you it's hot in here.

a. $K / k / q$

b. $k / K / T$

c. $T / \Delta G / \Delta H$

Key words:

Key equations:

"A Diamond is Forever" (DeBeers, 1947)

Advertising Age magazine named "A Diamond Is Forever" the best advertising slogan of the twentieth century (2000).



But it's just carbon!

ARE DIAMONDS FOREVER?

C (diamond) \rightarrow C (graphite)

<http://www.bris.ac.uk/Depts/Chemistry/MOTM/diamond/diamond.htm>

http://commons.wikimedia.org/wiki/File:Carbon_basic_phase_diagram.png

Properties: very hard, heat conductor, wide bandgap, high optical dispersion

History of Diamonds <http://www.amnh.org/exhibitions/diamonds/>

Synthetic diamonds <http://pubs.acs.org/cen/coverstory/8205/8205diamonds.html>

There are two bottles of acid of the same concentration.
One acid has a large pK_a ; the other has a small pK_a .
Someone will give you a lot of money if you submerge your
hand in one of the acids.
Which acid would you dunk your hand? Why?



Re-phrase the second sentence in “normal” English.

Explain what happens when a can of soda is opened. Give chemical reasons. How can you keep the soda from going flat?



<http://www.clipartbest.com/soda-can-images>

Sugar is used to preserve home-made jam and jelly by killing bacteria that may cause botulism. The appropriate sugar concentration will allow water to pass out of the cell and collapse (crenation) the cell. Should the sugar concentration that is used to preserve the jam be higher or lower than the sugar concentration inside bacteria cells? Give reasons.



Marble is calcium carbonate. Is CaCO_3 soluble in water? What numerical quantity tells you this information? Give the numerical value of this quantity to support your answer.

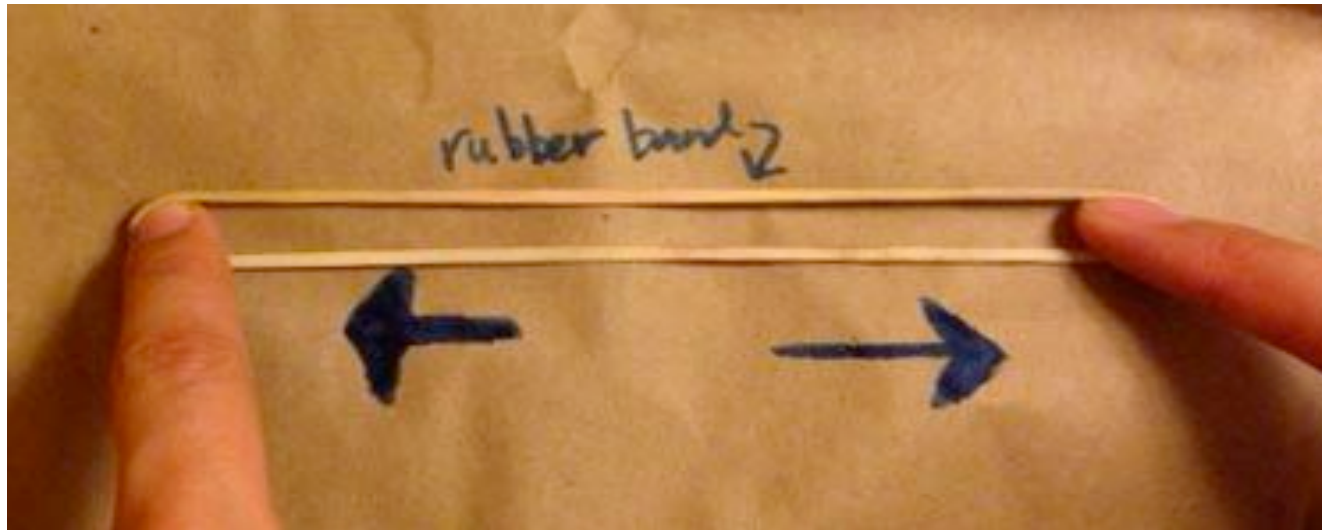


<http://en.wikipedia.org/wiki/Marble>

What observation tells you acid reacts with marble? Write a chemical equation that represents the reaction between marble and acid. Use HCl for the acid.

You hold a thick rubber band to your upper lip and quickly stretch it. Your lip feels warm.

Rubber band (unstretched) \rightarrow Rubber band (stretched)



<https://www.quora.com/What-is-happening-on-the-molecular-level-when-you-stretch-a-stretchy-object-such-as-a-rubber-band>

Is $\Delta H > 0$ or < 0 ?

Is $w > 0$ or < 0 ?

Is $\Delta G > 0$ or < 0 ?