Chemistry 332
Basic Inorganic Chemistry II

Instructor. Dr. Jon Veinot (Office E4-23, email jveinot@ualberta.ca)
Lectures. MWF 8:00 am

Textbook. G.E. Rodgers, Descriptive Inorganic Chemistry,
and Solid State Chemistry, 2nd Ed.

Grading.

Term Test I (Wednesday *February 9*, in class)	17%
Term Test II (Wednesday *March 9*, in class)	18%
Final Exam (Monday April 26, 9:00 am)	**35%**
Laboratory	30%
	100%

Deferred Exam. Monday May 2, 2005. 9:00am

Problem Assignments. Distributed periodically and will **NOT** be collected for evaluation.

Office Hours. Regular Weekly Hours T and Th 2:00-3:00pm
M,W,F 9:00am-5:30pm feel free to make an appointment.

Laboratory Details

Laboratory Coordinator. Dr. Jason Cooke W1-44

You need….

- Inorganic Chemistry 332 Laboratory 2004 Manual
- Safety Glasses
- One Card (to obtain supplies)

If you want to walk on water you have to get out of the boat!!

Think about the amoebas!!!

“ When teachers want students to grow, they don’t give them answers - they give them problems! … It is only in the process of accepting and solving problems that our ability to think creatively is enhanced, our persistence is strengthened, and our self-confidence is deepened.

If someone gives {you} the answers to the the test, {you} may get a good score on the test, but {you} have NOT grown.”

From John Ortberg’s “If you want to walk on water you’ve got to get out of the boat.”

Course Outline

I. Introduction to Transition Metal Complexes.

Classical complexes (Jorgenson and Werner)
Survey of ligand coordination numbers, geometries and types of ligands
Nomenclature
Isomerism

II. Bonding in Transition Metal Complexes.

Electron configuration of transition metals
Valence bond theory
Crystal field theory
Simple Molecular Orbital Theory
Electronic Spectra and Magnetism

III. Kinetics and Mechanisms of Inorganic Reactions.

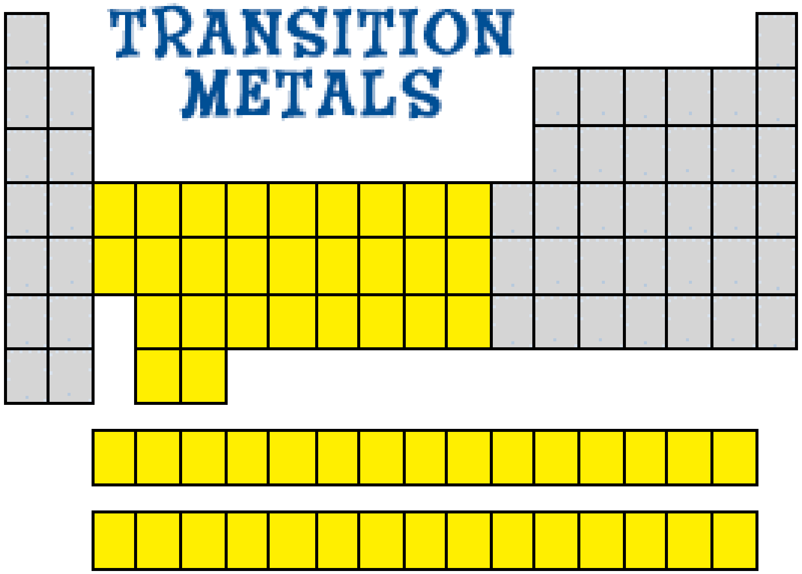
Stability and lability
Substitution reactions
Electron transfer reactions

IV. Descriptive Chemistry of TMs.

V. Organometallic Chemistry

18 e^- rule, σ, and π bonding ligands (synergistic bonding)
Metal carbonyls, synthesis, structure, reactions
Compounds with delocalized π-conjugated organic ligands.
Reactions and catalysis

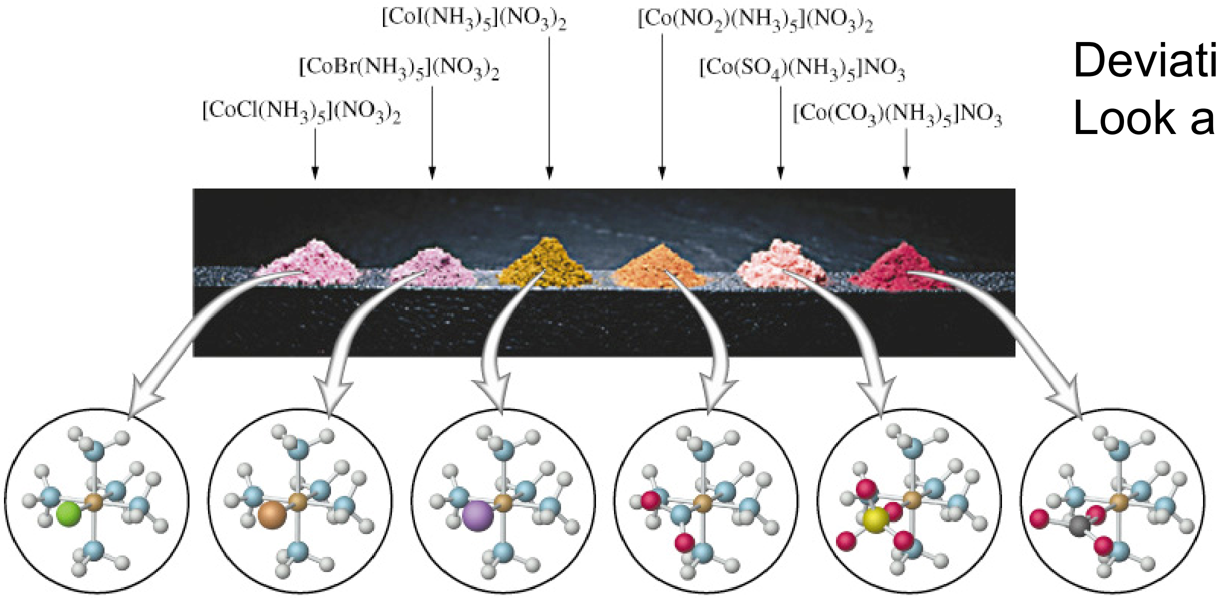
Where are transition metals on the periodic table?



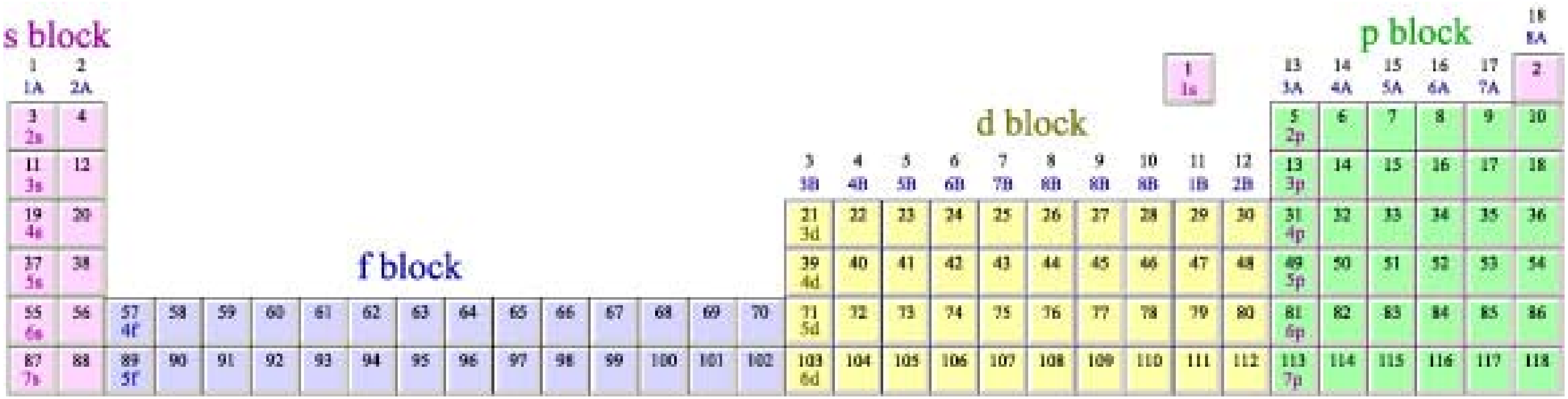
All of these elements have **partially filled *d* or *f* shells** in their elemental form or in any of their common oxidations states.

A general approximation for d-block elements involve the progressive filling of the d-orbitals.

Deviations exist to this pattern. Look at the Cr and Ni triads.



Electron configurations of TMs



d- block elements anomalies are indicated in **red**

Row 1	*Row 2*	*Row 3(filled 4f)*
Sc [Ar]$4s^2$ $3d^1$,	Y [Kr]$5s^2$ $4d^1$,	
Ti [Ar]$4s^2$ $3d^2$,	Zr [Kr]$5s^2$ $4d^2$,	Zr [Xe]$6s^2$ $5d^2$,
V [Ar]$4s^2$ $3d^3$,	Nb [Kr]$5s^2$ $4d^3$,	Ta [Xe]$6s^2$ $5d^3$,
Cr [Ar]$4s^1$ $3d^5$,	**Mo [Kr]$5s^1$ $4d^5$,**	**W [Xe]$6s^2$ $5d^4$,**
Mn [Ar]$4s^2$ $3d^5$,	Tc [Kr]$5s^2$ $4d^5$,	Re [Xe]$6s^2$ $5d^5$,
Fe [Ar]$4s^2$ $3d^6$,	**Ru [Kr]$5s^1$ $4d^7$,**	**Os [Xe]$6s^2$ $5d^6$,**
Co [Ar]$4s^2$ $3d^7$,	**Rh [Kr]$5s^1$ $4d^8$,**	**Ir [Xe]$6s^2$ $5d^7$,**
Ni [Ar]$4s^2$ $3d^8$,	**Pd [Kr]$5s^0$ $4d^{10}$,**	**Pt [Xe]$6s^1$ $5d^9$,**
Cu [Ar]$4s^1$ $3d^{10}$,	**Ag [Kr]$5s^1$ $4d^{10}$,**	**Au [Xe]$6s^1$ $5d^{10}$,**
Zn [Ar]$4s^2$ $3d^{10}$,	**Cd [Kr]$5s^2$ $4d^{10}$,**	**Hg [Xe]$6s^2$ $5d^{10}$,**

Row 4 are primarily not naturally occurring.

You MUST know the exceptions!

Valence Electrons in TM compounds

This is VERY important!

A general rule for TM compounds:

The valence electron configuration of M^{X+} is **d^n= NVE - oxidation state**

$CrCl_2$: Cr^{2+} **d^n= NVE - oxidation state = 6-2=d^4** **IT IS NOT $3d^34s^1$**

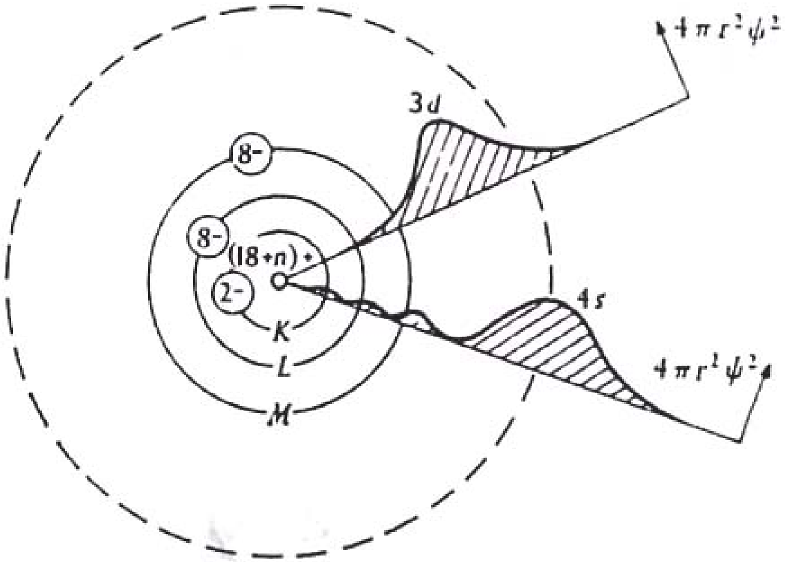
$CrCl_3$: Cr^{3+} **d^n= NVE - oxidation state = 6-3=d^3**

$Cr(CO)_6$: Cr^0 **d^n= NVE - oxidation state = 6-0=d^6**

**Does this look intriguing? Cr is “zero valent” like Cr metal!
But it also has an electron configuration of d^6.**

$[CoCl_4]^-$: Co^{3+} **d^n= NVE - oxidation state = 9-3=d^6**
$[Re_2Br_8]^{2-}$: Re^{3+} **d^n= NVE - oxidation state = 7-3=d^4**

Why only d-electrons?



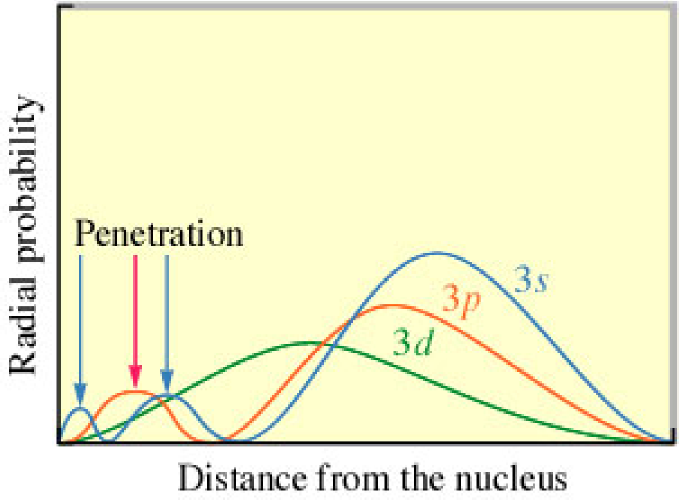
Very simply the relative energies of the n*d*, (n+1)*s*, and (n+1)*p* orbitals.

What do you already know from 331?

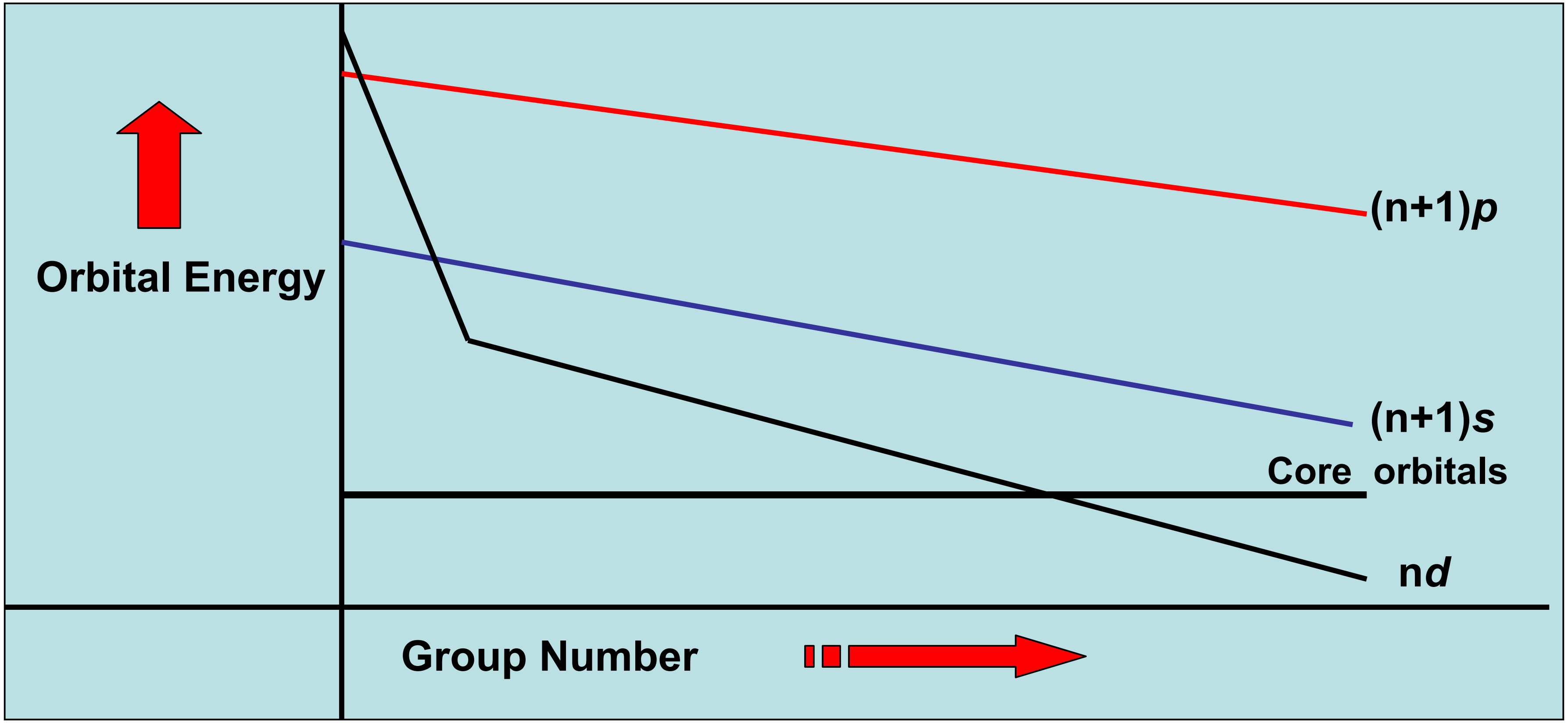
Generally, Z_{eff} increases across the periods **WHY?**

BUT THE Z_{eff} CHANGE AFFECTS THE n d-ORBITALS MORE THAN (n+1) s and p.

They are closer to the nucleus.



d-orbital energy



The orbital energy of a n*d* orbital decreases faster than that of the (n+1)*s* which in-turn decreases faster than the (n+1)*p* when going across the period.

This is implied by what we see in the electron configuration of Ga; [Ar $3d^{10}$]$4s^2 4p^1$. For Ga the $3d^{10}$ are part of the "core". This means the electron configuration of Ga mirrors that of B and Al, "s^2p^1"

Physical Properties of TMs

1. Almost all TMs are hard, ductile, malleable, high melting, and exhibit high electrical and thermal conductivities.

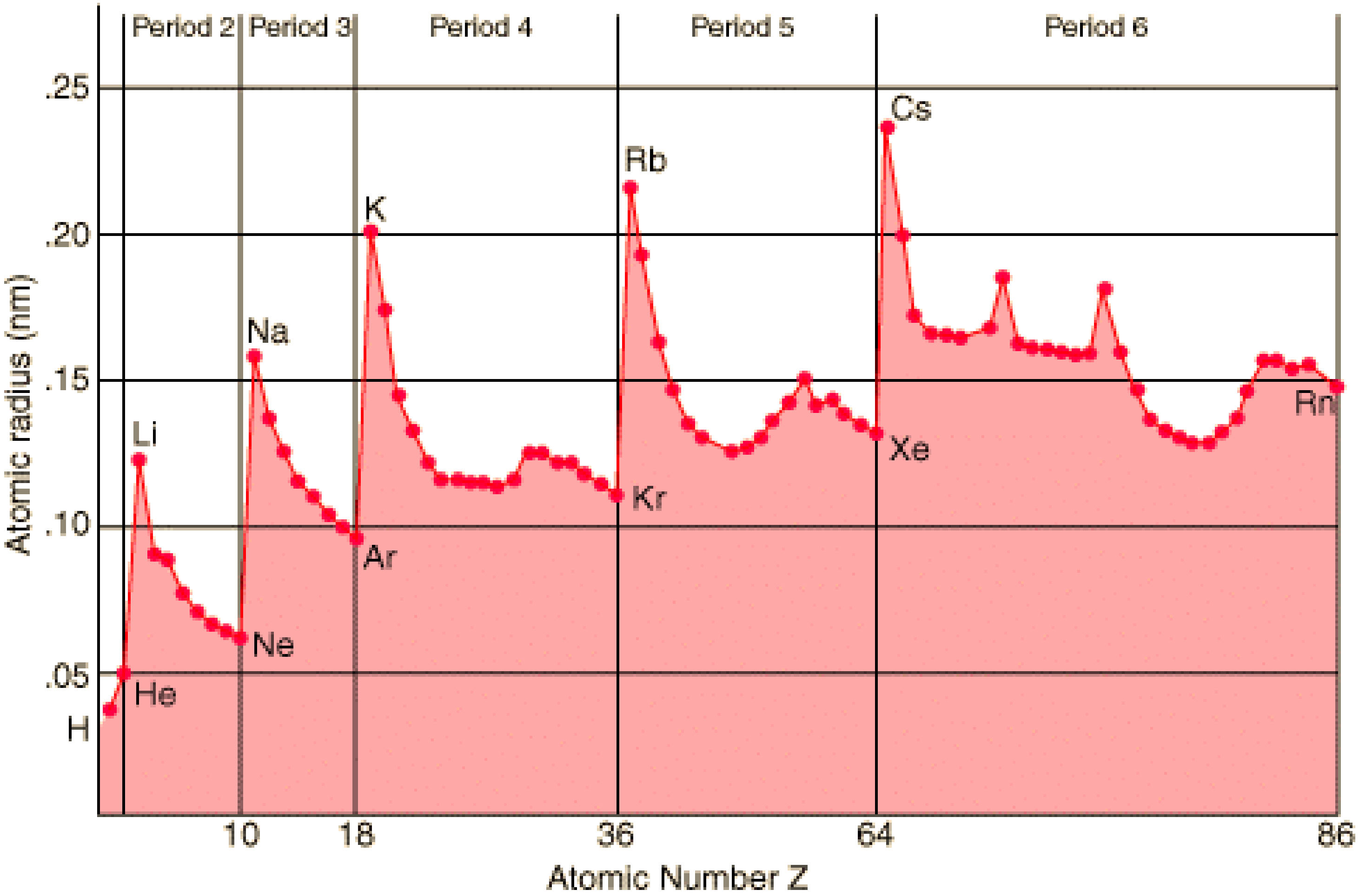
2. Relative to Group I and II metals TMs are much HARDER and less VOLITILE. The heats of atomization (ΔH_{atom}) are much higher than other main group metals.

Important experimental observation:

ΔH_{atom} (row 2 and 3 TMs) > ΔH_{atom} (row 1 TMs)

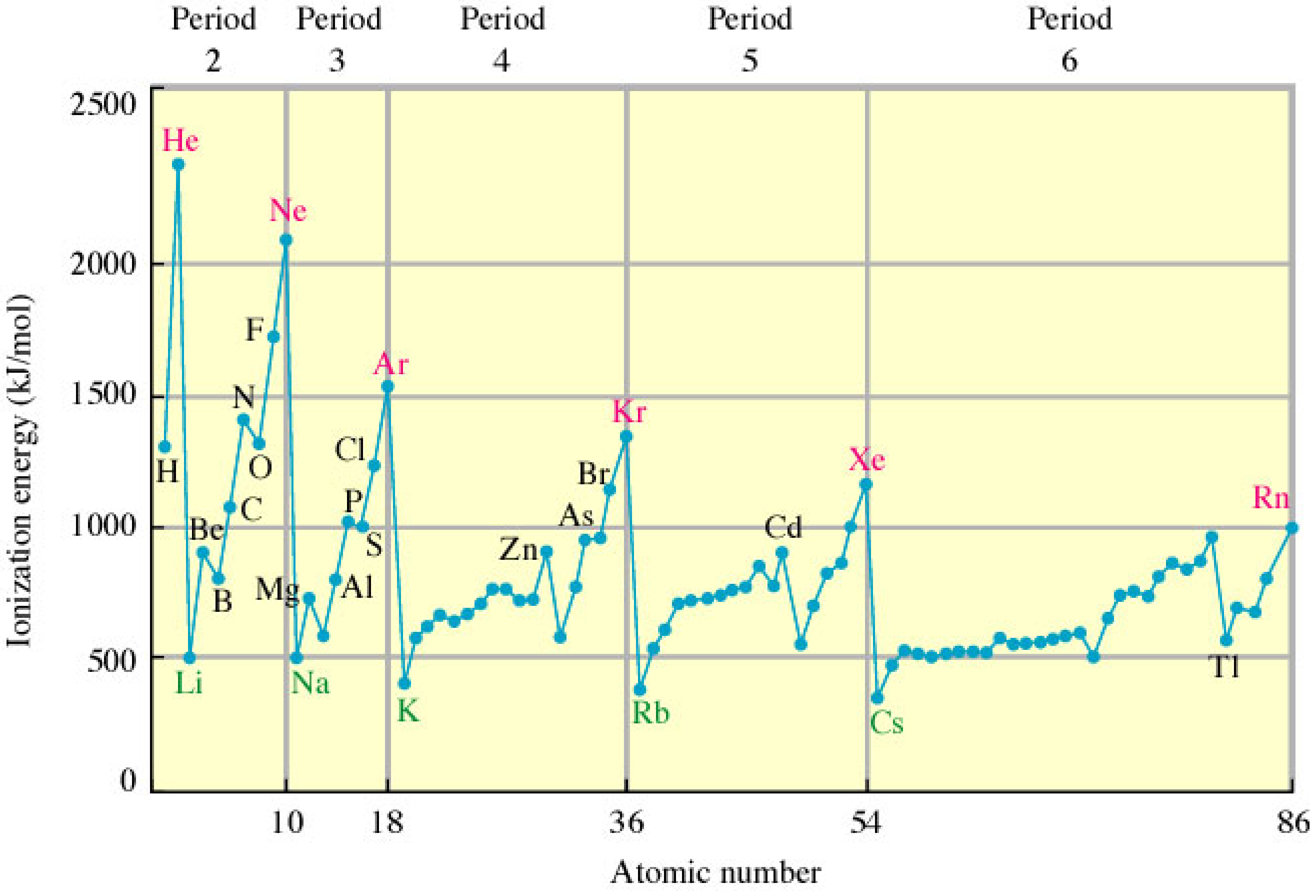
THIS IS IMPORTANT IN ACCOUNTNG FOR THE INCREASED PROPENSITY FOR M-M BONDING IN COMPOUNDS OF HEAVY TMs.

TM Atomic Radii



TMs have smaller radii than Group I and II metals. There is a decrease in size with increased atomic number but not as dramatic as see for main group metals.

TM 1st Ionization Energies



IE$_1$ of TMs are higher than Group 1 and 2 metals but vary far less than those of typical elements (look at K through Kr).

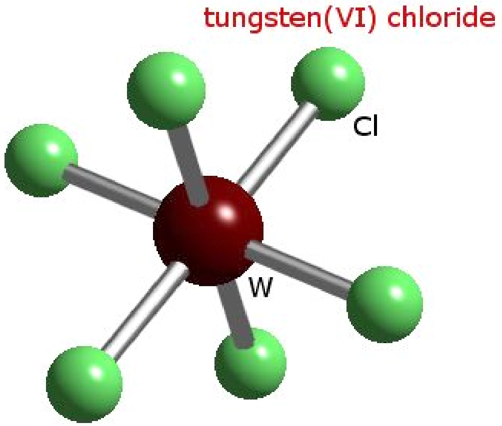
IE increases with Z across a period with small variations (don’t worry about them)

Chemical Properties of TMs

Given the high ΔH_{atom} and IE of TMs they tend to be less reactive than Group II metals. Yet, they will react with O_2, S, and halogens if they are heated with these elements.

$$W_{(s)} + 3Cl_{2(g)} \xrightarrow{600^{o}C} WCl_{6(s)}$$

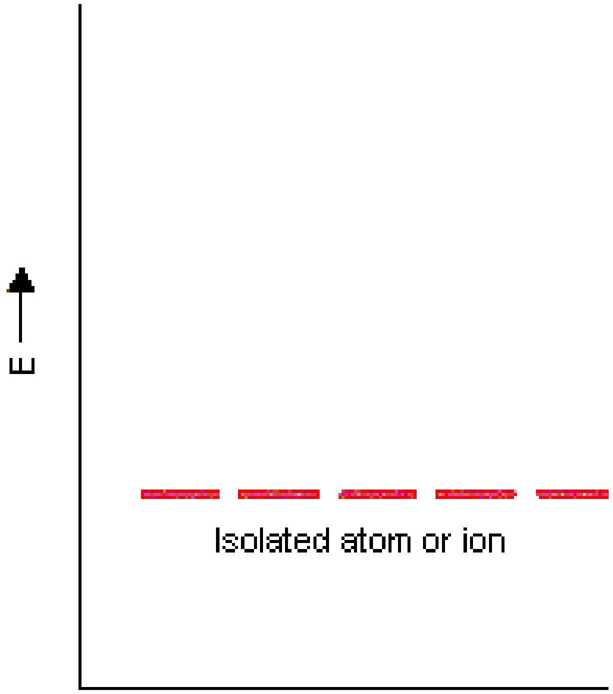
Blue-black crystals



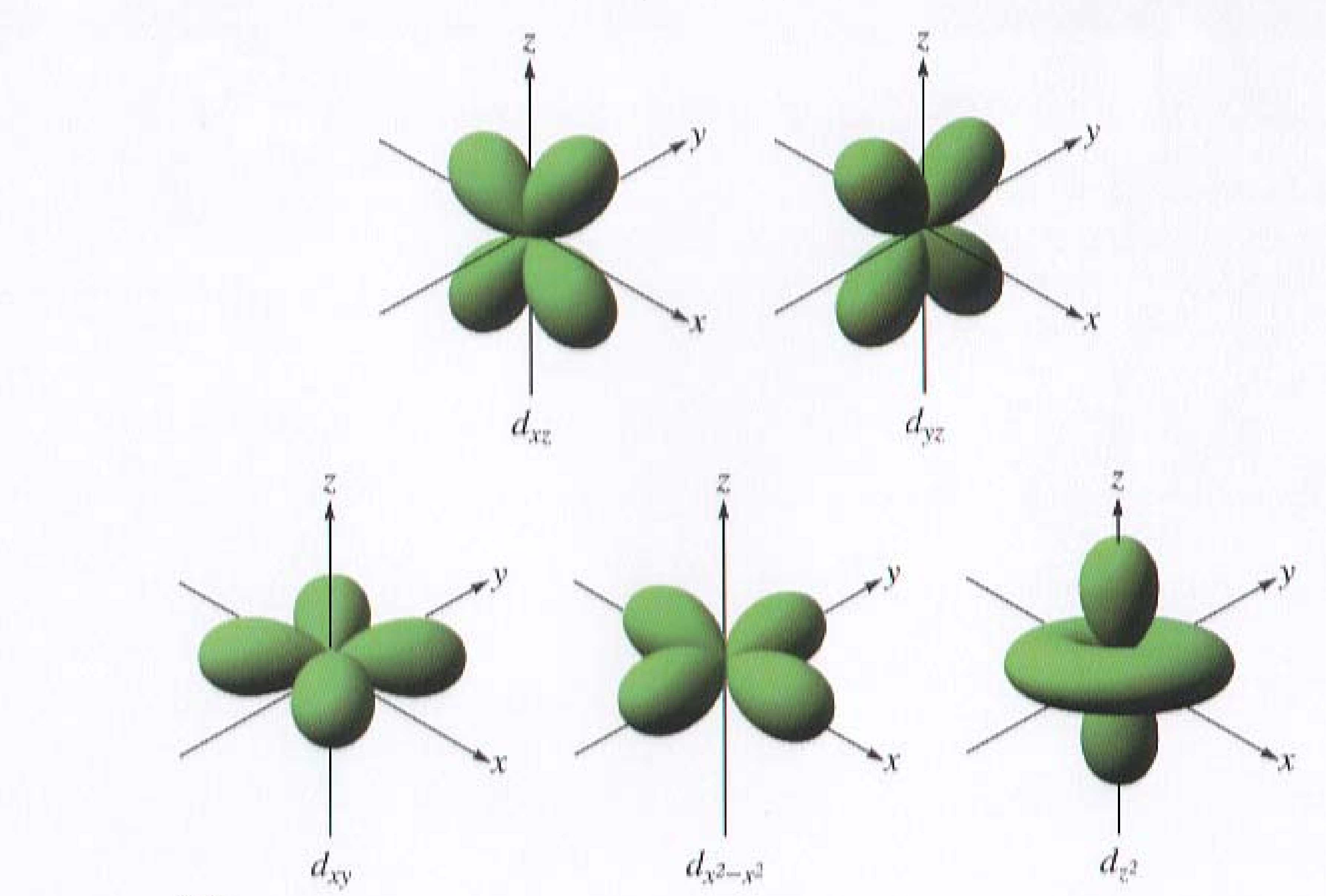
TM compounds

TM compounds are often coloured. Colours originate from electronic transitions between different d-orbitals of the same principle QN.

Wait….aren't all d orbitals the same energy?

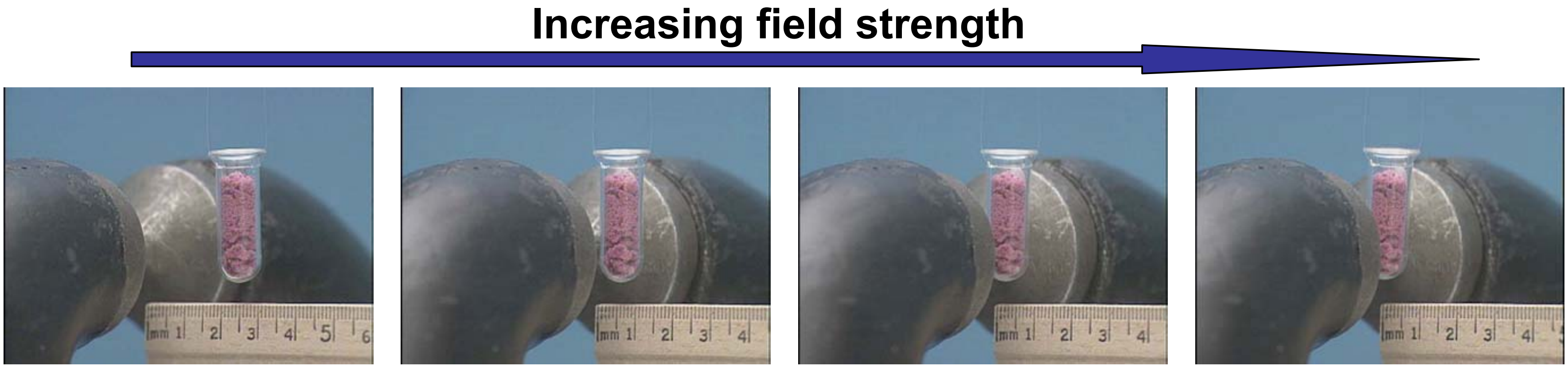


d-Orbitals



TM magnetism

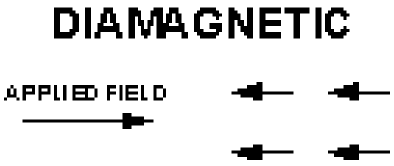
Many TM compounds are **paramagnetic**: this is because of partially filled d-orbitals and the resulting unpaired electrons.

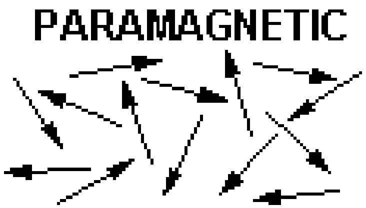


Cobalt(II) chloride hexahydrate

3 unpaired electrons which align their spins with a large applied magnetic field and are drawn into it.

For a more complete discussion on magnetism see handout later.

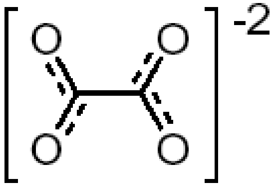




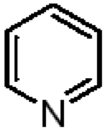
# of UPE is commonly measured experimentally using a Gouy Balance, NMR spectroscopy.

More on this later.

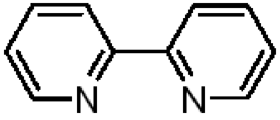
TMs have a wide range of reactivity



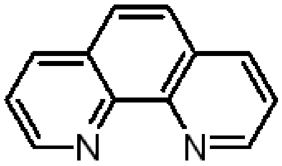
oxalate, "ox"



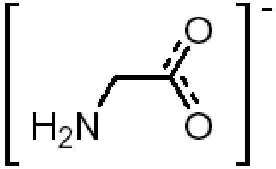
pyridine, "py"



bipyridine, "bpy"



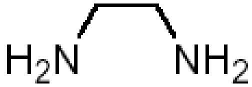
phenanthroline, "phen"



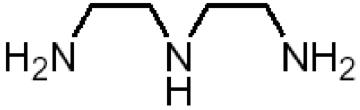
glycinate, "gly"

TMs are Lewis acids and will accept electrons from Lewis bases.

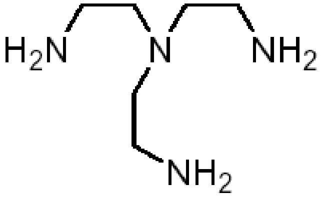
We refer to these Lewis bases as ligands. (Latin, "to tie or bind")



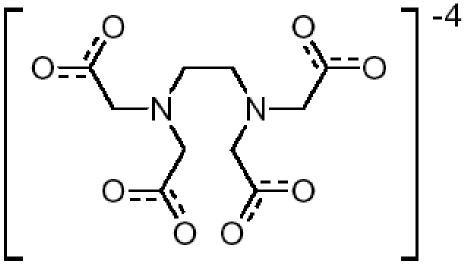
ethylenediamine, "en"



diethylenediamine, "dien"



triethylenediamine, "tren"



ethylenediamine tetraacetate, "edta"

TM oxidation states

TMs have numerous available oxidation states. This is VERY important as it sets apart their chemistry from the main group elements.

It is also very difficult to discuss this comprehensively.

Generalities:

i) Early and Late Transition metals have few oxidation states.

- **Early TMs have very few *d* electrons to loose.**
- **Late TMs have high Z_{eff} and loss of electrons is difficult.**

ii) High oxidation state TMs tend to form covalent molecules rather than simple ionic salts.

High oxidation states are most stable for 2nd and 3rd row TMs.

Examples of the influence of TM oxidation states.

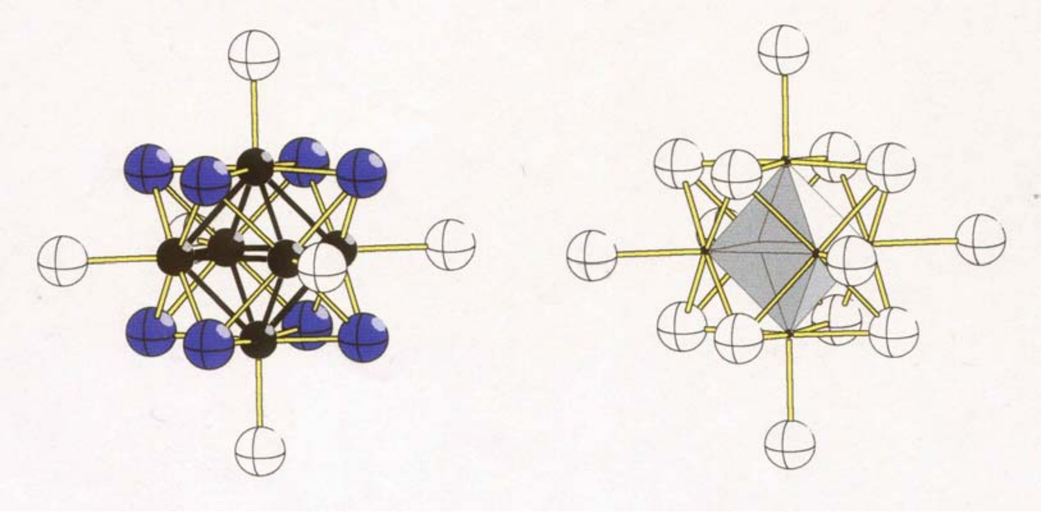
$TiCl_2$ and $TiCl_3$ are solids like $SnCl_2$, $TiCl_4$ is a molecular liquid like $SnCl_4$. Mn_2O_7 is an explosive oil but Re_2O_7 melts at 220°C and OsO_4 is a volatile solid. The latter two compounds are covalent substances and the +7 and +8 oxidation states are “formal”.

TM oxidation states con’t

iii) The Chemistry of 1st row TMs is dominated by M^{2+} and M^{3+} ions. There is extensive solution chemistry involving redox equilibria, complex formation, and precipitation.

iv) The Chemistry of 2nd and 3rd row TMs is not as straightforward.

-lower oxidation states are dominated by M-M interactions (“$MoCl_2$” below)



- High oxidation states form molecular species and covalent bonds.
- Aqueous Chemistry is complicated and rarely involves simple, monoatomic species.

Ligands and TM Oxidation States

Ligands that stabilize low oxidation states.

Two common ligands tend to favor metals of low ox. State.
Carbon monoxide (CO) and the isoelectronic cyanide ion (CN^-)

(a detailed discussion of M-CO bonding will follow shortly)

Ligands that stabilize "normal" oxidation states.

Most ligands fall into this category.

Ligands that stabilize HIGH oxidation states.

Think back to the fluorine complexes of Xe….this will help you understand. Generally TMs will adopt high Ox. States if they are coordinated to fluoride or oxide ions.

Coordination Chemistry

Rodgers Chapter 2

These compounds are challenging to chemists…hence the term complex has come to be associated with them.

These compounds appear to violate the rules of “valence”.

An example of the puzzlement.
Let’s go back to 1800 when Tassaert and Fremy studied Co(II) reacting with NH_3.

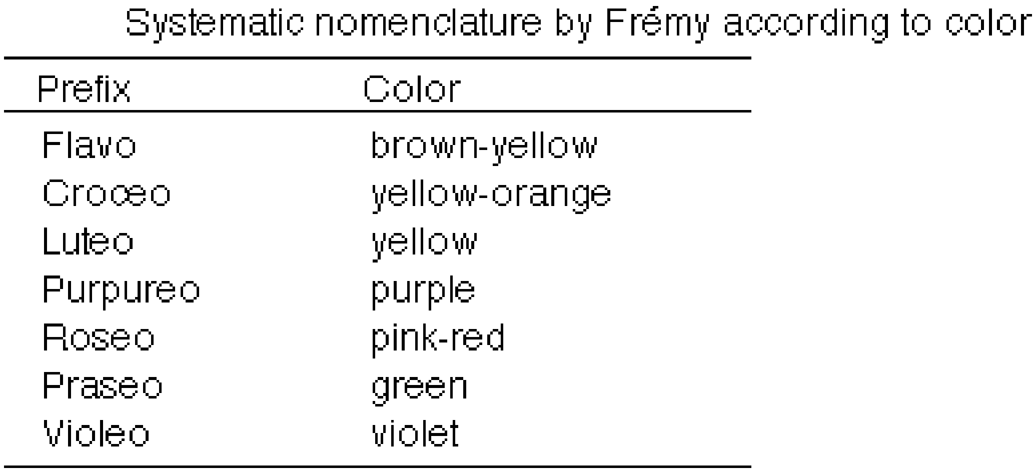
$$CoCl_{2(aq)} \xrightarrow{\mathbf{NH_3\ and\ air}} \text{brown} \xrightarrow{\mathbf{heat}} \text{red orange product}$$

Fremy successfully demonstrated that Co(II) was oxidized to Co(III) but there were $6NH_3$ molecules associated with each Co.

Questions arise….

Chemical Controversy

$$CoCl_{2(aq)} \xrightarrow{NH_3 \text{ and air}} \text{a lot of coloured products}$$



Systematic nomenclature by Frémy according to color

Prefix	Color
Flavo	brown-yellow
Crocœo	yellow-orange
Luteo	yellow
Purpureo	purple
Roseo	pink-red
Praseo	green
Violeo	violet

ca. 1870 Kettentheorie (**Blomstrand** and **Jørgensen**)
based on Valence numbers

Sophus Mads Jorgensen, Professor at the University of Copenhagen

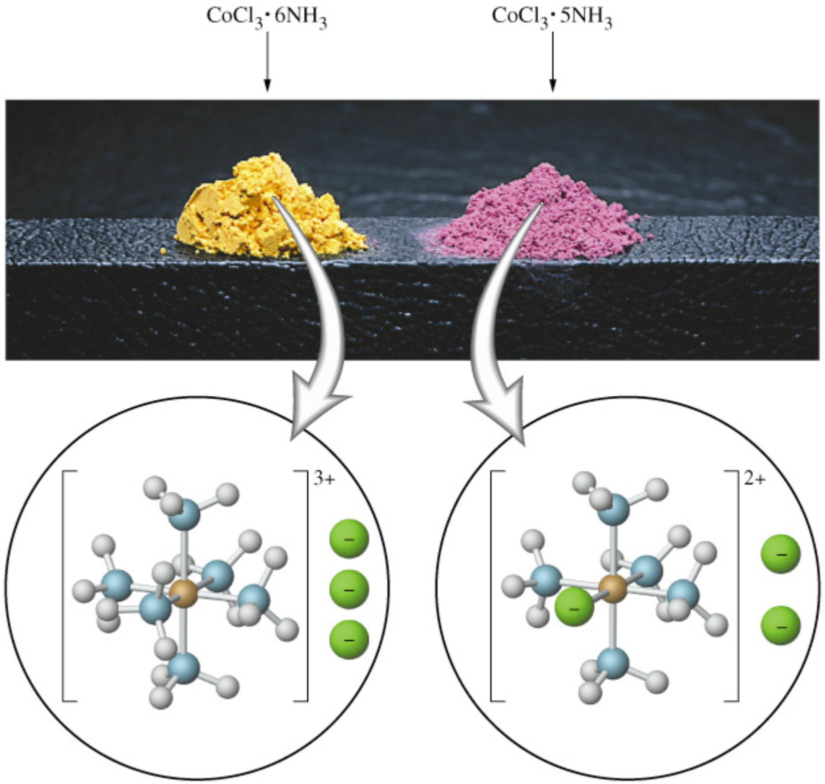
Alfred Werner

$$[Co(NH_3)_6]Cl_3(s) \xrightarrow{H_2O(l)} [Co(NH_3)_6]^{3+}(aq) + 3\,Cl^-(aq)$$

Golden orange

$$[CoCl(NH_3)_5]Cl_2(s) \xrightarrow{H_2O(l)} [CoCl(NH_3)_5]^{2+}(aq) + 2\,Cl^-(aq)$$

Purple



Werner developed his theory of coordination chemistry at the age of 26, received the 1913 Nobel Prize for chemistry and in 25 years supervised 200 PhD students and published syntheses for in excess of 8000 complexes.

How does Werner’s work manifest itself now?

I. Every metal of a particular *Oxidation State* has a definite *Coordination Number*.

The oxidation state is “satisfied” or “balanced” by the presence of anions.

The coordination number can be is “satisfied” not only by the presence of anions, but also by electron-pair donating, neutral molecules like N, O, S, P.

THIS SHOULD LOOK FAMILIAR!

The **oxidation state** of a metal center is defined by its electronic configuration.

The **coordination number** of a metal center is defined as the number of atoms directly bonded to the metal center.

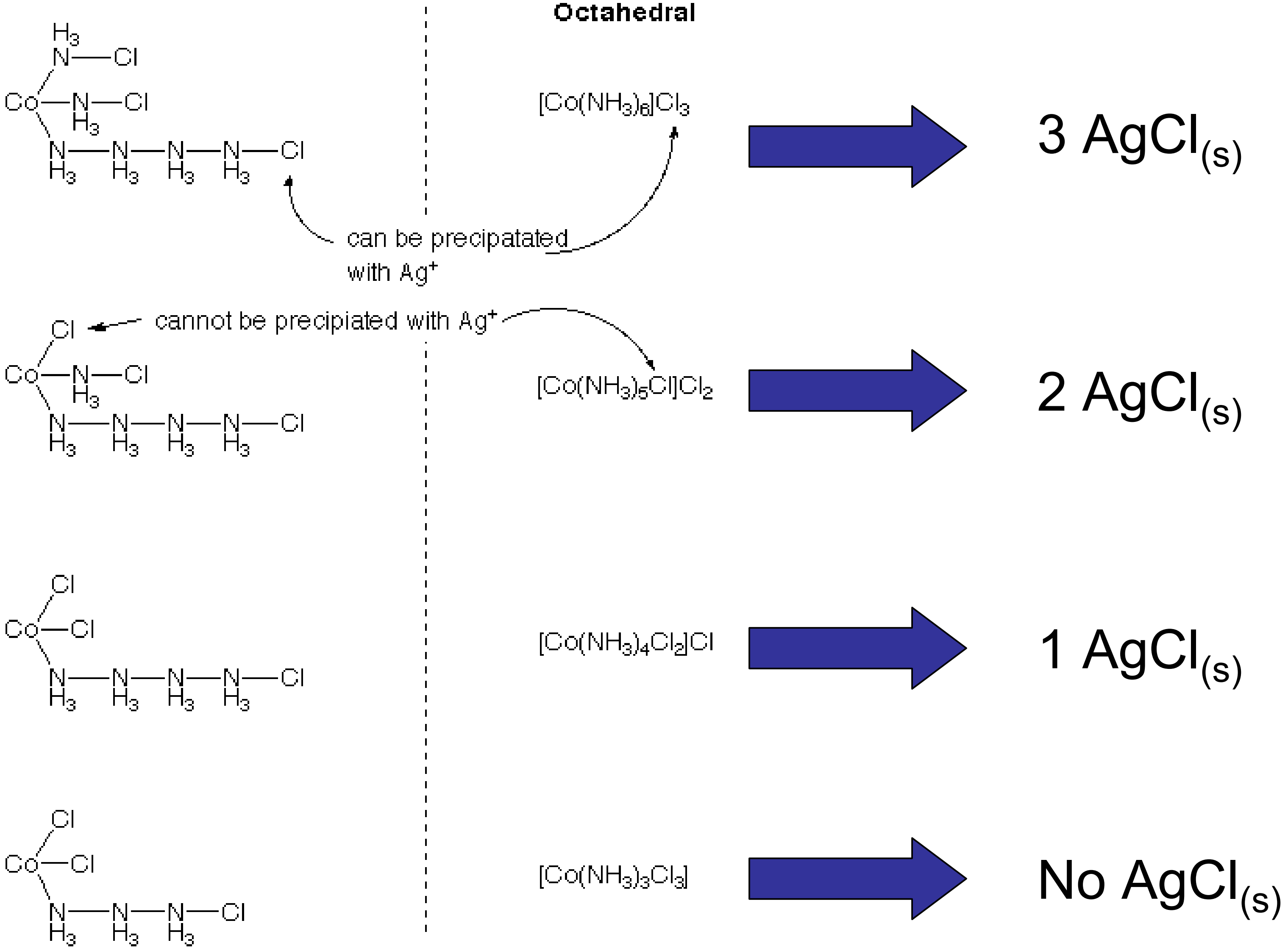
This portion of the theory may be viewed as the “constitution” of a coordination compound

II. The bonds of ligands are “fixed” in space.

This postulate gives rise to fixed geometric structures of coordination compounds and the possibility of isomers.

This portion of the theory may be viewed as the “configuration” of a coordination compound

Comparing the approaches

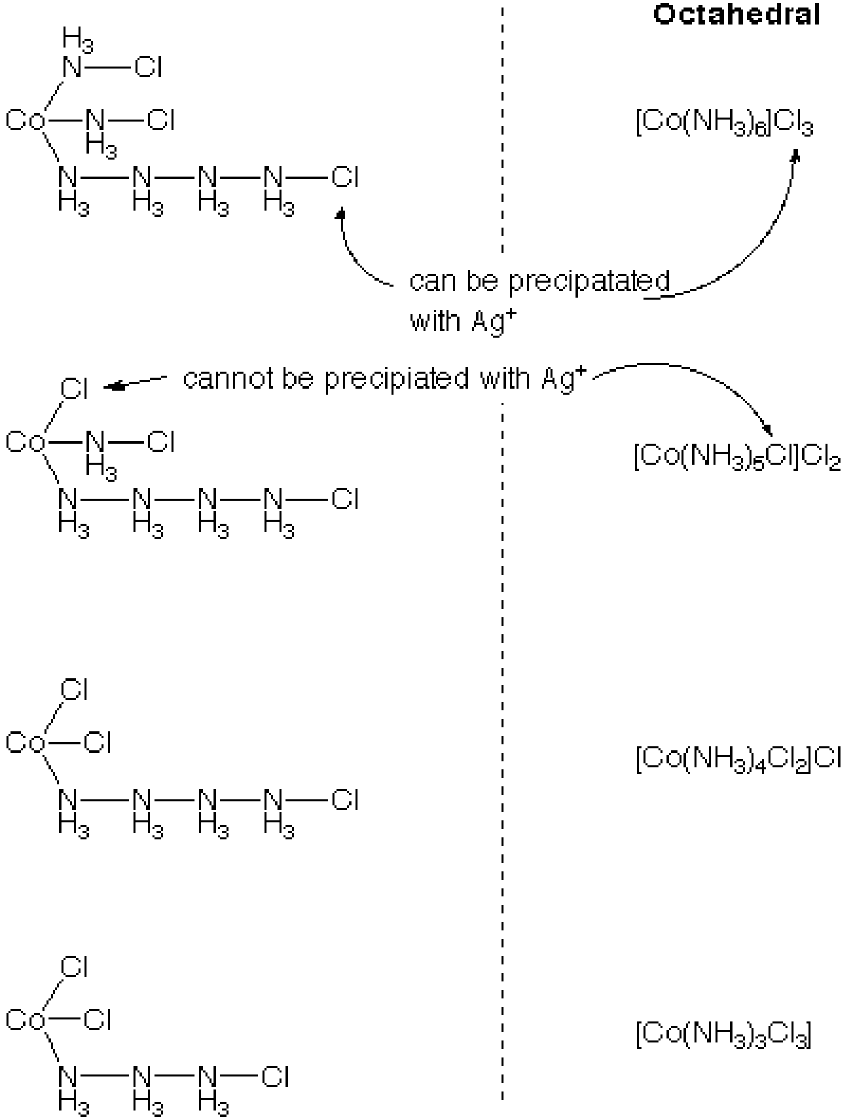


Jorgensen	Werner Octahedral	Experimental observation with XS $AgNO_{3(aq)}$
$Co(NH_3Cl)(NH_3Cl)(NH_3NH_3NH_3NH_3Cl)$	$[Co(NH_3)_6]Cl_3$	3 $AgCl_{(s)}$
$Co(Cl)(NH_3Cl)(NH_3NH_3NH_3NH_3Cl)$	$[Co(NH_3)_5Cl]Cl_2$	2 $AgCl_{(s)}$
$Co(Cl)(Cl)(NH_3NH_3NH_3NH_3Cl)$	$[Co(NH_3)_4Cl_2]Cl$	1 $AgCl_{(s)}$
$Co(Cl)(Cl)(NH_3NH_3NH_3Cl)$	$[Co(NH_3)_3Cl_3]$	No $AgCl_{(s)}$

How else could this have been tested

Jorgensen

Werner



Octahedral

$[Co(NH_3)_6]Cl_3$

can be precipatated with Ag^+

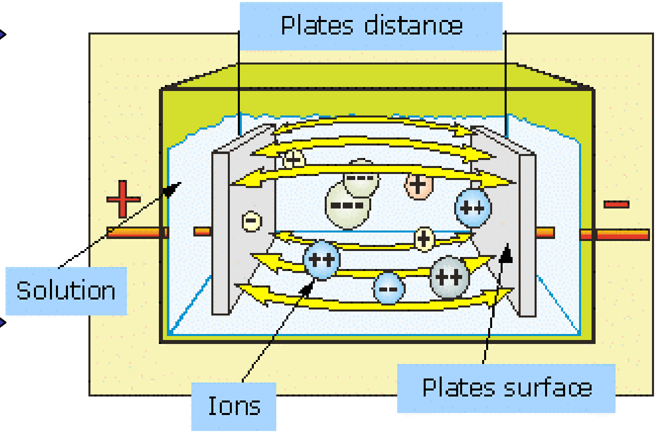
cannot be precipiated with Ag^+

$[Co(NH_3)_5Cl]Cl_2$

$[Co(NH_3)_4Cl_2]Cl$

$[Co(NH_3)_3Cl_3]$

How many ions are present?



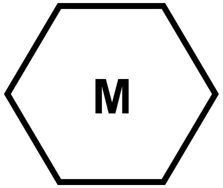
The solution resistance (inverse of conductivity) is proportional to plate area, ionic concentration, plate separation, and ionic charge.

Configuration in coordination compounds and isomer counting

How can we explain that there are two different complexes with the formula $[CoCl_2(NH_3)_4)]^+$

One is **GREEN**……the other is **VIOLET**

What if the complex of the formula ML_4X_2 was planar?

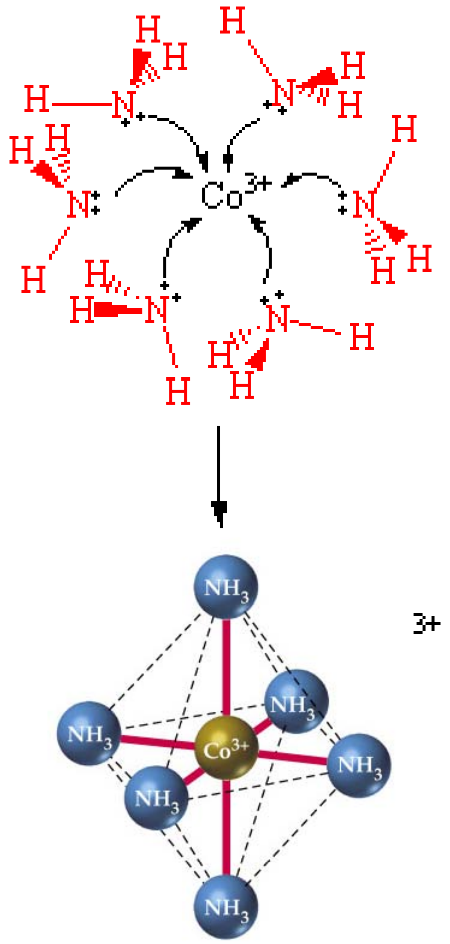


Not all the ligands are equivalent how many orientations will there be?

Why do these complexes form?

Recall that based upon the work of Lewis and Sidgwick a chemical bond requires the “sharing” of an electron pair.

Acid (LA) : electron pair acceptor **Base (LB): electron pair donor**



From this it can be drawn that metals behave as Lewis acids and Ligands as Lewis bases.

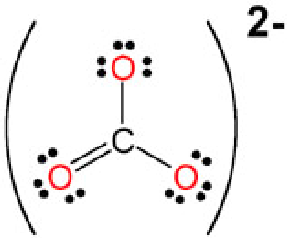
A bond like that seen in $[Co(NH_3)_6]^{3+}$ is a “coordinate-bond” or “dative-bond”. This used to be denoted with $\longrightarrow$. This is no longer the case.

This is because there is no fundamental difference between a “coordinate-bond” and a polar covalent bond.

Yet there is a difference in that a **covalent bond undergoes homolytic cleavage** and a **dative bond undergoes hetrolytic cleavage.**

Typical Monodentate Ligands

F^-	fluoro
Br^-	bromo
I^-	iodo
CO_3^{2-}	carbonato
NO_3^-	nitrato
SO_3^{2-}	sulfito
$S_2O_3^{2-}$	thiosulfito
SO_4^{2-}	sulfato
CO	carbonyl
Cl^-	chloro
O^{2-}	oxo
O_2^{2-}	peroxo
OH^-	hydroxo
NH_2^-	amido
CN^-	cyano
SCN^-	thiocyano
NO_2^-	nitro

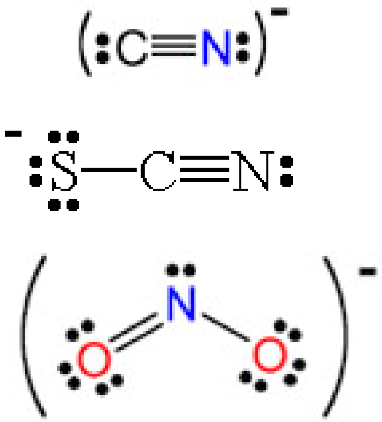


Can be bidentate

Common bridging ligands.

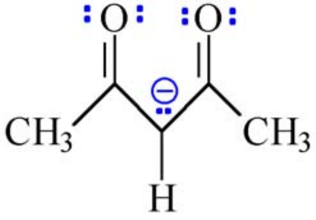
Common bridging ligands. That are also ambidentate.

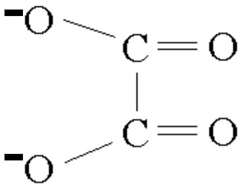
H_2O	aqua
NH_3	ammine
CH_3NH_2	methylamine
$P(C_6H_5)_3$	triphenylphosphine
$As(C_6H_5)_3$	Triphenyl arsine
N_2	dinitrogen
O_2	dioxygen
NO	nitrosyl
C_2H_4	ethylene
C_5H_5N	pyridine



Typical multidentate ligands


ethylenediamine (en)

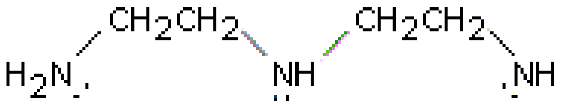

acetoacetonato (acac)


oxalato (ox)

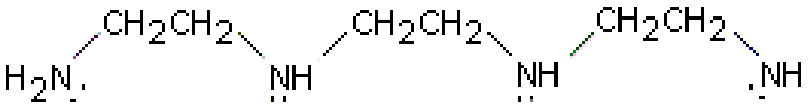
$NH_2CH_2COO^-$

glycinato (gly)

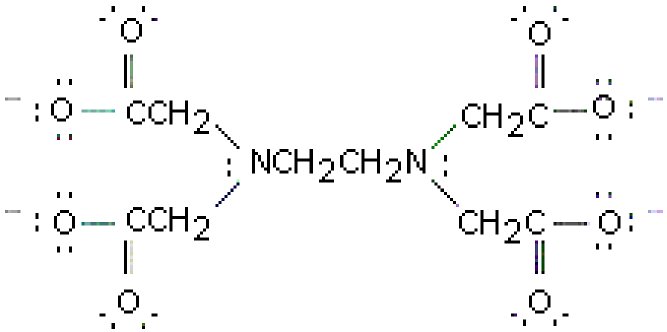
Tridentate Ligand:


diethylenetriamine (dien)

Tetradentate Ligand:


triethylenetetraamine (trien)

Hexadentate Ligand:


ethylenediaminetetraacetate (EDTA)

Ligand Nomenclature Rules

1. Anionic ligands all end in -*o.*

2. Neutral Ligands are named as the neutral molecule.

3. There are some special names for neutral ligands.

4. Cationic ligands end in *-ium.*

5. Ambidentate ligands are indicated by:
   i) using special names for the two forms (nitro $-NO_2^-$ and nitrito -O-NO)
   ii) placing the symbol for the coordinating atom in front of the ligand name (s-thiocyanato or N-thiocyanato).

6. Bridging ligands are indicated by placing μ- before the ligand name.

Examples of these rules may be found on your handout.

Rules for Simple Coordination Compounds

1. Name the cation first, then the anion.

2. List the ligands alphabetically.

3. Indicate the number (2,3,4,5,6) of each type of ligand by:
   - The prefixes di, tri, tetra, penta, hexa for:
     - a) All monoatomic ligands.
     - b) Polyatomic ligands with short names.
     - c) Neutral ligands with special names.

   - The prefixes bis, tris, tetrakis, pentakis, hexakis for:
     - a) Ligands whose names contain a prefix of the first type (di, tri, etc.)
     - b) Neutral ligands without special names.
     - c) Ionic ligands with particularly long names.

4. If the anion is complex, add the suffix *-ate* to the name of the metal. (Often the -*ium* or other suffix of the normal name is removed prior to adding *-ate.* Some metals such as copper, iron, gold, and silver use the Latin stem names and become cuprate, ferrate, aurate, and argenate respectively.)

5. Put the ox. state in roman numerals in parentheses after the name of the central metal.

Examples of Naming

$[Co(NH_3)_5(OH_2)]Br_3$	amine x 5 water x 2	cobalt (III)	bromide
$[Co(NH_3)_5Br]Br_2$	amine x 5 bromine x 1	cobalt (III)	bromide
$[Co(NH_3)_5Br](SO_4)$	amine x 5 bromine x 1	cobalt (III)	sulfate
$([Co(NH_3)_5(SO_4)]Br)$	amine x 5 sulfate x 1	cobalt (III)	hydrogen sulfate

Pentaaminediaquacobalt (III) bromide

Pentaaminebromocobalt (III) bromide

Pentaaminebromocobalt (III) sulfate

Pentaaminesulfatocobalt (III) bromide

More examples can be found in Rodgers Chapter 2 P. 20-25.

Structural Isomerism

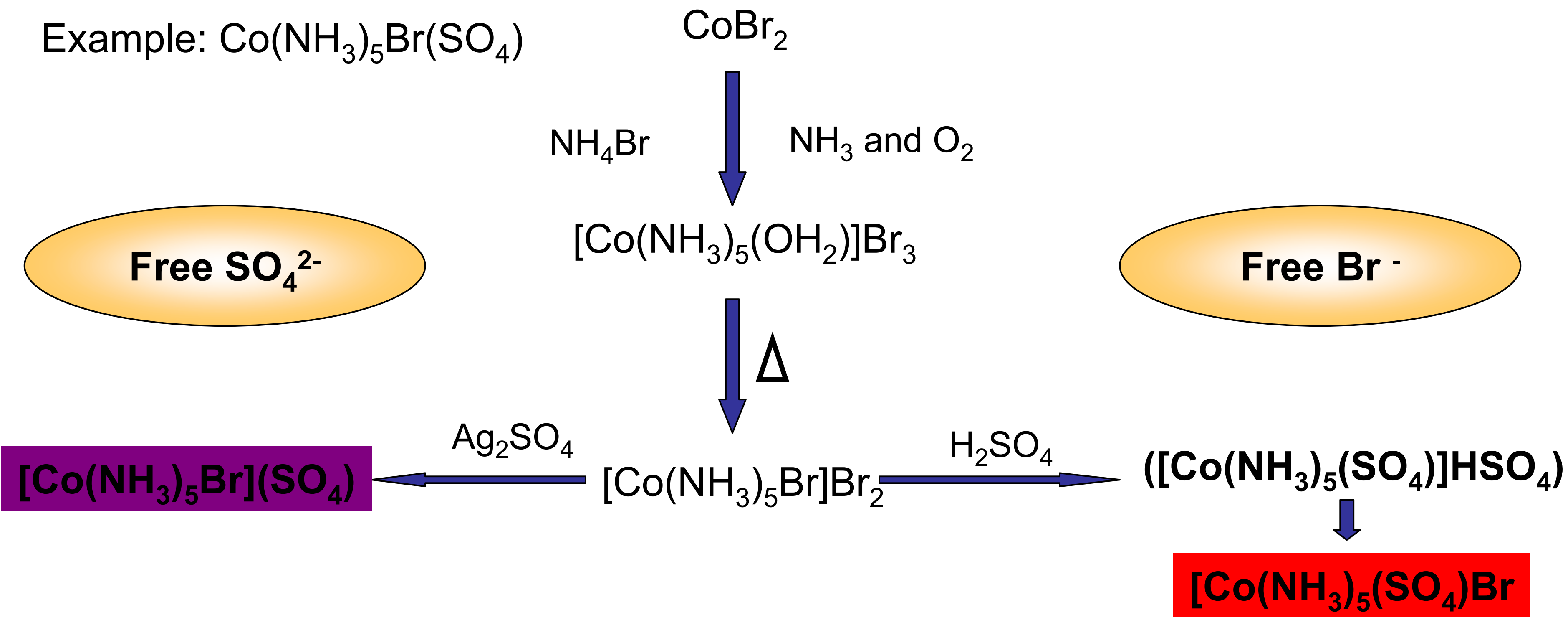
Definition. Structural isomers have the identical composition and differ in M-L linkages.

This class of isomers was crucial to the realization of Werner's premise regarding the constitution of coordination complexes.

Structural isomers may be divided into sub-classes of:
ionization isomers, *coordination isomers*, and linkage isomers.

Ionization isomers ***like hydration***: 2 different ions are obtained when dissolved in solution.

Example: $Co(NH_3)_5Br(SO_4)$



$CoBr_2$

NH_4Br

NH_3 and O_2

$[Co(NH_3)_5(OH_2)]Br_3$

Δ

Free SO_4^{2-}

Free Br^-

Ag_2SO_4

$[Co(NH_3)_5Br]Br_2$

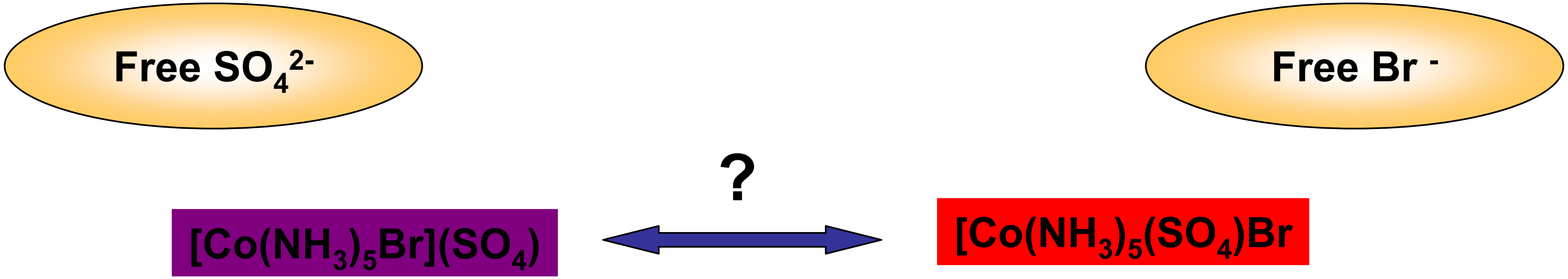
H_2SO_4

$[Co(NH_3)_5Br](SO_4)$

$([Co(NH_3)_5(SO_4)]HSO_4)$

$[Co(NH_3)_5(SO_4)Br$

How do we know the difference?



Free SO_4^{2-}

Free Br^-

?

$[Co(NH_3)_5Br](SO_4)$

$[Co(NH_3)_5(SO_4)Br$

Coordination Isomers

Coordination isomers are possible when both the anion and cation contain metal ions. As a result different distributions of ligands between metal centers result.

Two compounds are known that contain two Pt(II) ions, four ammonia molecules, and four chloride ions.
They are:

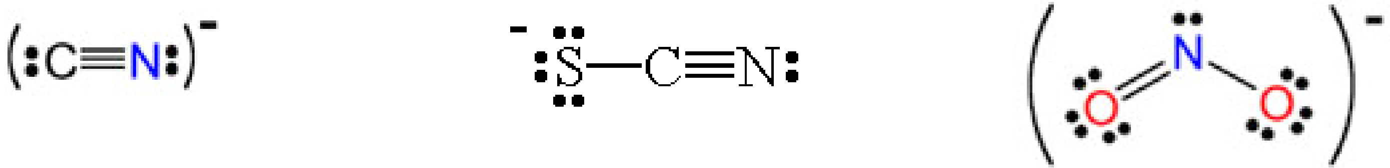
$\mathbf{[Pt(NH_3)_4][PtCl_4]}$ and $\mathbf{[Pt(NH_3)_3Cl][Pt(NH_3)Cl_3]}$

$[Pt(NH_3)_2Cl_2]$ has the **same ratio of atoms**, but does not have the same overall formula. It is not a coordination isomer of the above compounds.

$\mathbf{[Co(NH_3)_6][Cr(CN)_6]}$ and $\mathbf{[Cr(NH_3)_6][Co(CN)_6]}$

Linkage Isomers

Linkage isomers can exist when one or more ambidentate ligands is bonded to a metal ion.



This type of isomerization was discovered by Jorgensen in 1894.

$[Co(NH_3)_5Cl]Cl_2$

$$\Big\downarrow \; NH_3/HCl \qquad NaNO_2$$

Solution “A”

What’s going on?

$[Co(NH_3)_5\text{“}NO_2\text{”}]Cl_2$

The nitrite ion can bind in two different ways. Through the O or through the N.

What do the structures look like?

Jorgensen figured this out in 1894……BUT HOW?
He did not have IR-spectroscopy, X-ray crystallography, etc…

Was he correct?

How can you tell?

Isomerization Summary

Ionization Isomers. 2 different ions are obtained when dissolved in solution. (Same formula…..different solution species.)

This is similar to the Hydration, although in the case of HI isomers differ in the number of coordinated water molecules.

Coordination Isomers. When both the anion and cation contain metal ions different distributions of ligands between metal centers result.

Linkage Isomerism. Bonding of ligands through different modes. A good example of this involves the binding of $NO_{2.}$

Structure of Simple Coordination Compounds

A review of conventions for drawing 3-D structures on paper.

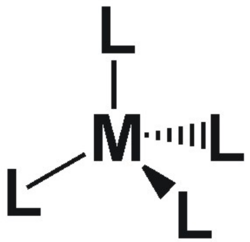
M-L bond in the plane of the page.

M-L bond out of the plane of the page.

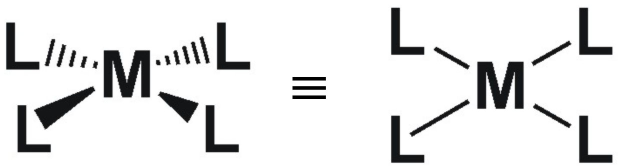
M-L bond into the plane of the page.

Four Coordinate Complexes

ML_4

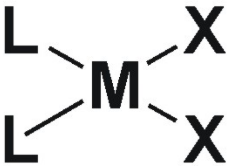


tetrahedral

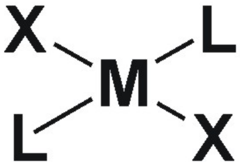


square planar

ML_2X_2



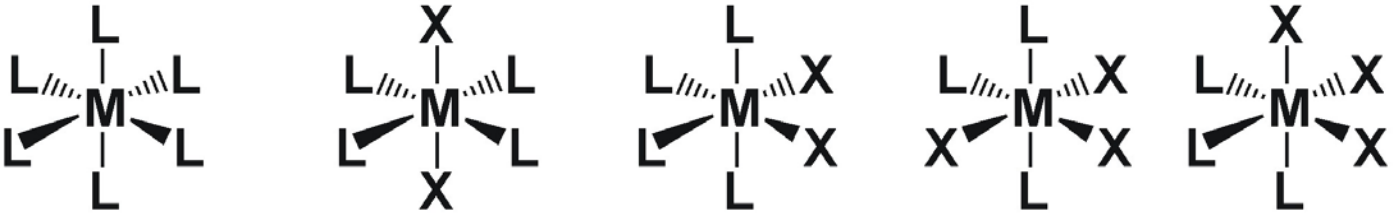
cis



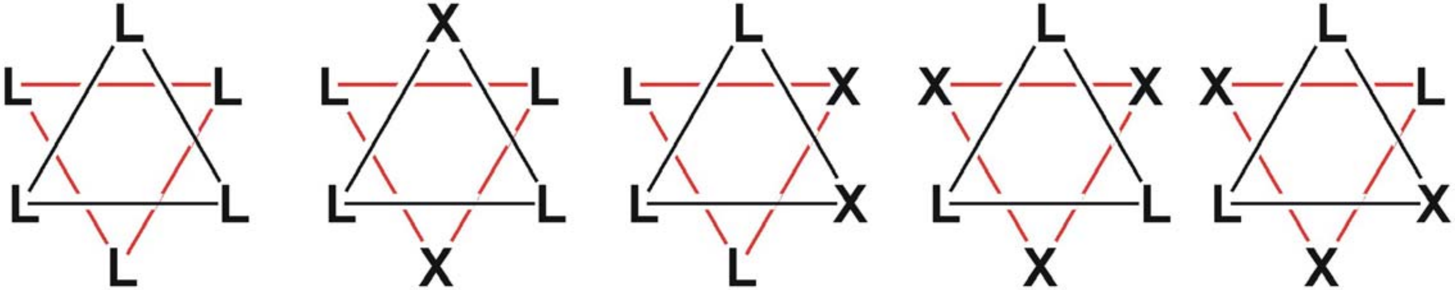
trans

Six Coordinate Complexes

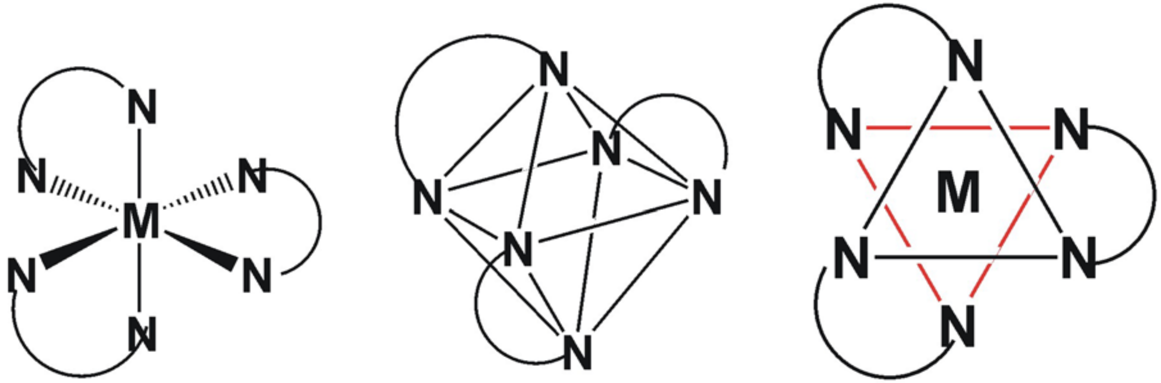
ML_6 **ML_4X_2** **ML_3X_3**



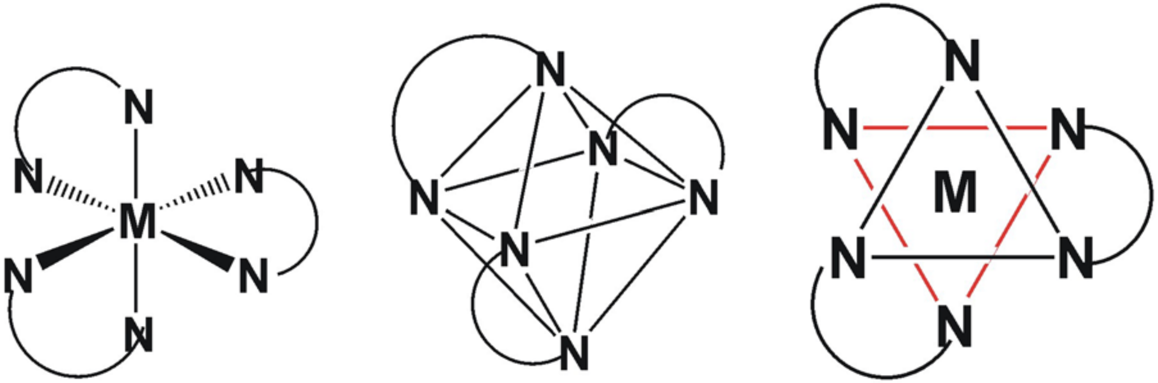
octahedral **trans-** **cis-** **facial (fac)** **meridianal (mer)**



These are the same complexes viewed down a face of the octahedron.



Tris-ethylenediamine Chelates



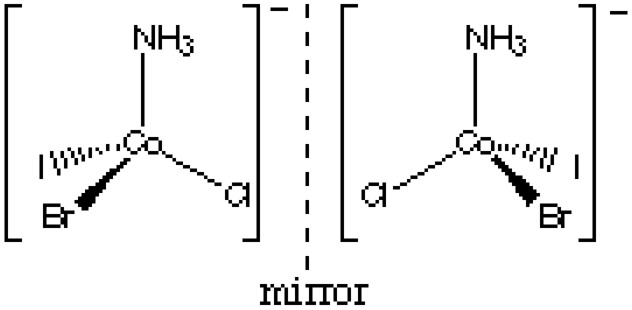
These are the structural representations of ONE optical isomer.

Understanding these structural formulae is crucial to you deciding on chirality.

Optical Isomerization

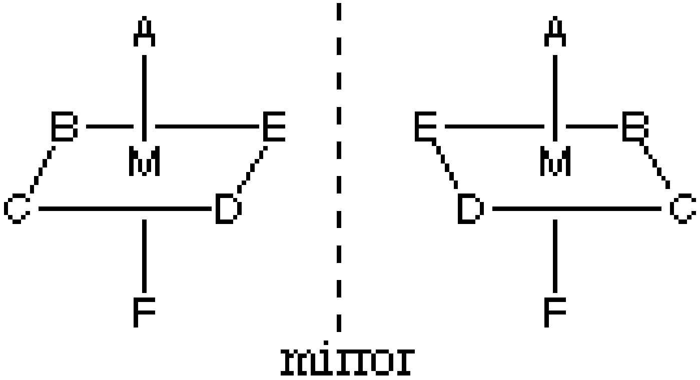
Tetrahedral Geometry

The $[Co(NH_3)ClBrI]^-$ ion is tetrahedral, with four different groups bonded to the cobalt. It has two nonsuperimposable mirror images:



This is the same as you see for organic chemistry.

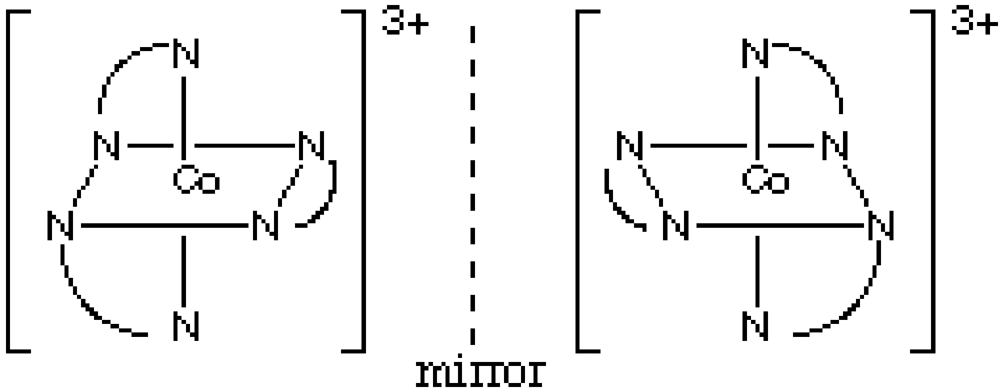
Octahedral Geometry

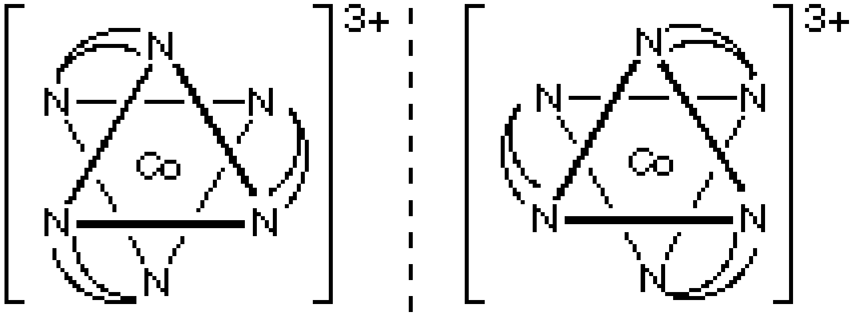


Similarly, an octahedral metal ion bonded to 6 different ligands would be chiral.

Optical Isomerization Con't

Chirality and optical isomerism that does not merely depend on having four different groups attached to a tetrahedral central atom. Tris(ethylenediamine)cobalt(III) ion is chiral, in spite of the fact that the three ethylenediamine ligands are all the same and are themselves symmetrical:





left-handed screw

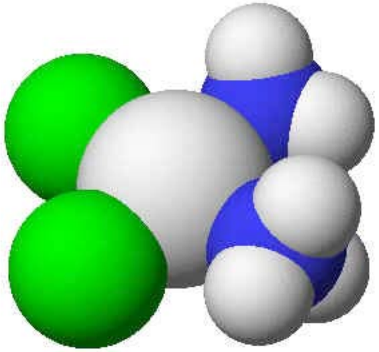
right-handed screw

cisplatin

$PtCl_2(NH_3)_2$

Diaminedichloroplatinum (II)

Cisplatin was first synthesized by M. Peyrone in 1844 and has been called Peyrone's chloride. Its structure was first elucidated by Alfred Werner in 1893.



The trans isomer $Pt(NH_3)_2Cl_2$ is therapeutically inactive.

It is possible to distinguish between isomers based on the activity of the two Pt-Cl bonds (expected around 300 cm^{-1} in the IR region). The vibrational spectra of these isomers differ, due to the different symmetries. The point group affiliations for the two isomers are different, and, as it turns out, so are the vibrational selection rules.

Discovery of Clinical application.

In the early 1960's, a series of experiments in the laboratories of Barnett Rosenberg at the Michigan State University found some peculiar results. An experiment designed to measure the effect of electrical currents on cell growth yielded Escherichia colithat were 300 times the normal length. This effect was not due to the electrical fields themselves but to a chemical agent that was formed in a reaction between the supposedly inert platinum electrodes and components of the solution. The chemical agent was later determined to be cisplatin.

Tests revealed the compound had prevented cell division, but not other growth processes in the bacteria. **It was approved for cancer treatment in 1978.**

Survey of Ligands

The most efficient method for classifying ligands is by structure.

Specifically, by the number of coordinate (dative) bonds they make with a central metal atom.

Monodentate. ***ONE*** donation per ligand. This literally means “one-toothed”.

Examples. These ligands may be neutral or anionic.

$:NR_3$, $:PR_3$, $(NR_2)^-$, $(PR_2)^-$, OR_2, SR_2, OR^- (including OH^-), O^{2-}, X^- (halides)

It is important to note that there is only **ONE** donor atom. BUT, when there are more than one L.P. available these ligands can bridge metal ions.

Note that this is different that in B_2H_6, here each bond is 2 center-2 electron.

Survey of Ligands

Polydentate. ***More than ONE*** donation per ligand.

Bidentate Ligands. (two donors, two teeth)

When these ligands bind to a single central metal they are said to be “chelating ligands”. (This arises from the Greek word for claw.)

Four membered rings. (See Experiment 4 for the different bonding modes of the carboxylate ligand.)

carboxylate

dithiocarbamates

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carboxylate

dithiocarbamates

Survey of Ligands

Bidentate Ligands. (two donors, two teeth) cont’d

Five membered rings.

ethylenediamine (en)

2,2’-bipyridine (bpy)

Six membered rings.

β-diketonates (acetylacetonate, acac)

salicylaldiminato (sal)

My favorite “bidentate” ligand.

Survey of Ligands

Polydentate. ***More than ONE*** donation per ligand.

Tridentate Ligands. (three donors, two teeth)

Diethylenetriamine

terpyridine (trpy)

Hydrotris(pyrazolyl) borates (TpRR’)

Quadradentate

porphyrin

Survey of Ligands

Penta- and higher dentate Ligands.

The most well known hexadentate ligand is ethylenediaminetetraacetate ($EDTA^{4-}$). It can be protonated and be a pentadentate ligand. ($EDTAH^{3-}$).

$EDTA^{4-}$

$EDTAH^{3-}$

Other examples include:

Crown Ethers

Cryptates

15-crown-5

dibenzo-18-crown-6

Electronic Classification of Ligands

Ligands can be classified in terms of their electronic characteristics and their interaction with a metal center.

Classical or Simple donors. All ligands must be able to donate an electron pair to the metal center (the Lewis acid) to form a σ-bond. These ligands are also known as σ-donors.

$:NH_3$ and OH_2

π- donors. If a ligand has *more than one electron pair* to donate to the metal center it can form a *σ-bond* (as above) and if it has the ability to donate more electrons through **π-donation**.

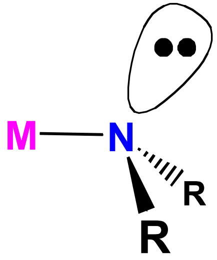
Without question *these ligands can stabilize high oxidation state metal centers*. M^{x+} will be electron deficient and has empty dπ orbitals to accommodate the extra ligand electrons.

^{-}OR, $^{-}NR_2$, $^{-}N{=}N{-}R$

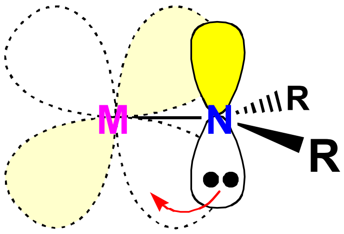
O^{2-}, N^{3-} these are strong π-donors

Electronic Classification of Ligands

π**- donors.** The orbital picture.



2e- donor
pyramidal geometry



4e- donor
trigonal planar

π**-acid ligands.** These ligand donate one electron pair in a σ-bond (as above) and the ability to accept back metal electrons through π**-donation**.

In this case the electrons are clearly coming from the metal center and the metal center MUST be electron rich.

R_3P: (P has an empty d orbital)

:C≡O (empty π* orbital)

Draw the orbital cartoon!

Recall the HSAB concept of CHEM331. (R-C pp. 141-149; 450-451).

What Should a Bonding Theory Explain?

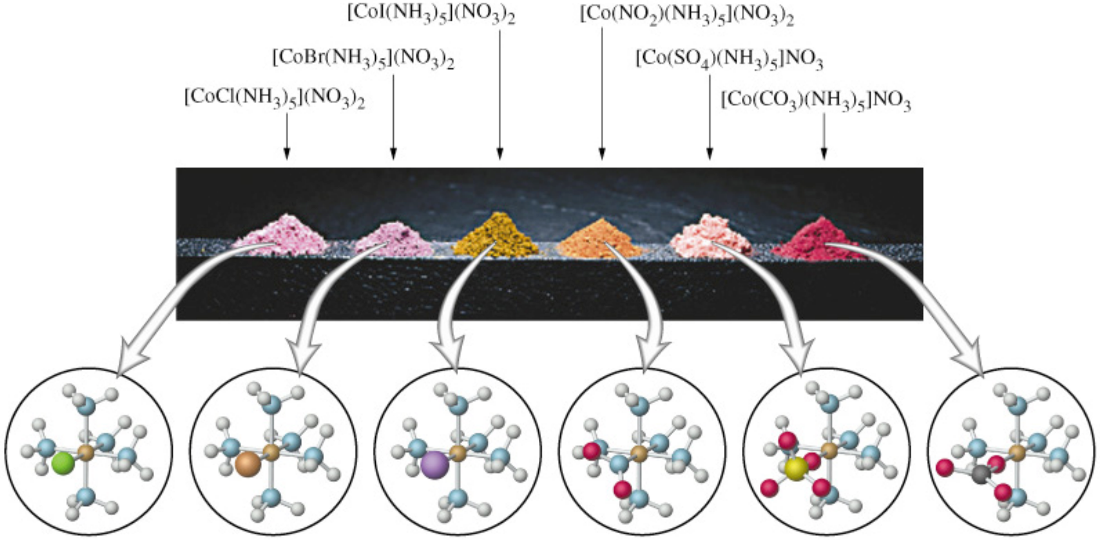
In our intro have already outlined some of the properties of transition metal complexes. For a bonding theory to be effective it must address these points.

You already have some understanding of Lewis structures and VSEPR theory…. They don’t fit the bill.

Where do they fall down?

I. Colours of Transition Metal Complexes

Why are most transition metal complexes brightly coloured but some aren't?
Why do the colours change as the ligand changes?
Why do the colours change as the oxidation state of the metal changes, even for complexes of the same ligand?



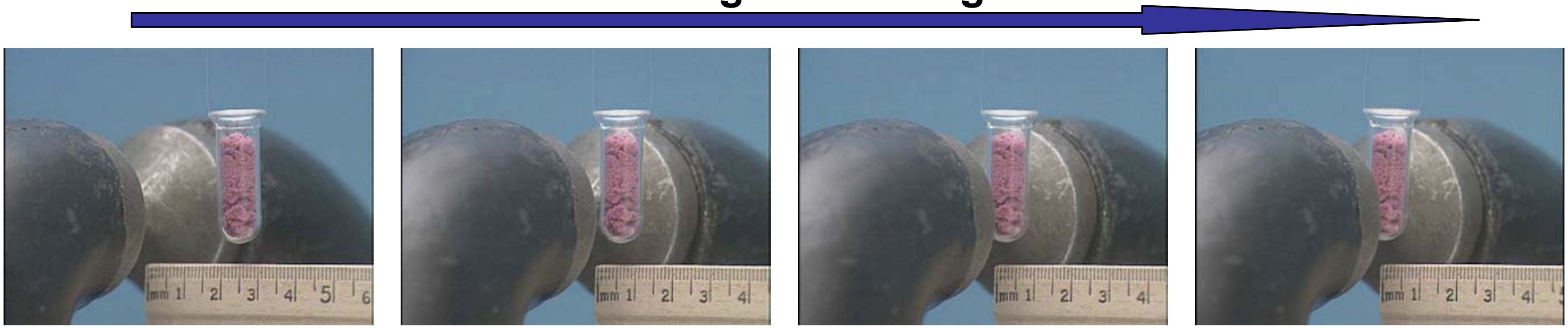
What Should a Bonding Theory Explain?

The Magnetic Moment of a Complex and the Number of Unpaired Electrons

How can we determine the number of unpaired electrons…..

This is important before we define our theory of bonding.

Increasing field strength

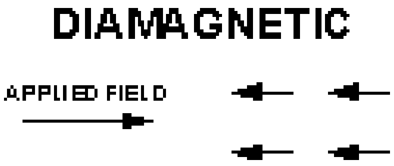


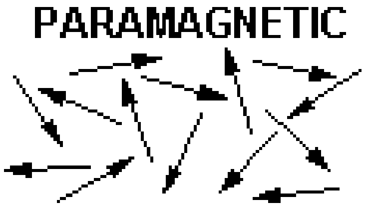
Cobalt(II) chloride hexahydrate

3 unpaired electrons which align their spins with a large applied magnetic field and are drawn into it.

For a more complete discussion on magnetism see R-C p. 14-15

paired e^-





unpaired e^-

Handling magnetic data

One approach is to use a Gouy balance is used to measure the mass of a sample with and without being exposed to a strong magnetic field.

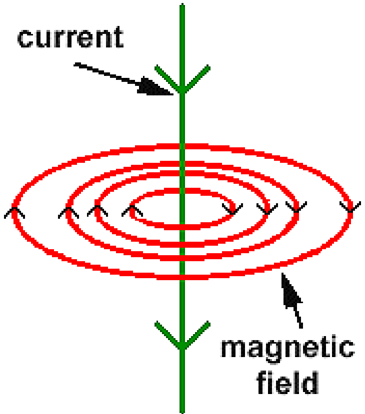
The difference in mass can be used to calculate the ***magnetic susceptibility*** of the sample, and from the magnetic susceptibility the ***magnetic moment*** can be obtained.

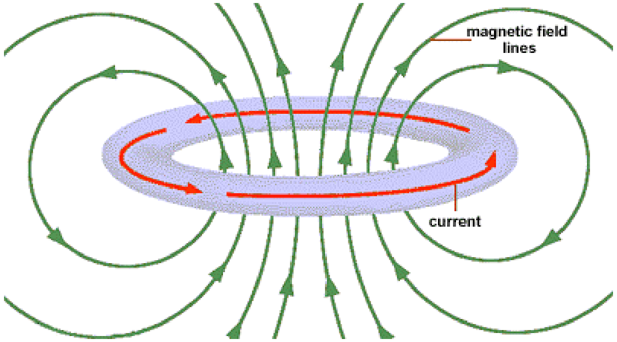
$$\mu = 2.84\sqrt{\chi_M T}$$

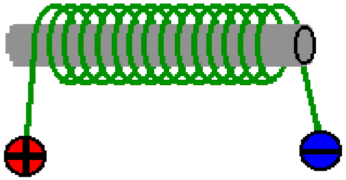
μ = magnetic moment in Bohr magnetons (B.M.)
χ_M = magnetic susceptibility
T = absolute temperature

(note: χ_M is the molar susceptibility and is the mass susceptibility (χ_g) multiplied by the molecular mass M.)

Where does the magnetic moment come from?



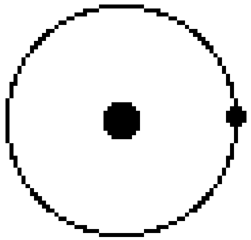




Molecular magnetic moment

The magnetic susceptibility and thus the magnetic moment are due to moving charges.
Just like the coil of wire on the previous transparency.

In an atom, the moving charge is an electron



electron spinning on its axis ↿ or ⇂ gives the spin magnetic moment

electron moving in its orbital creates an additional magnetic field, leading to the orbital magnetic moment

For first row transition metals, the affect of the **orbital magnetic moment is negligible.**

This means that the measured magnetic moment can be directly related to the ***number of unpaired electrons*** **(n)** in the ion. This value is called the **spin-only magnetic moment**, and its units are **Bohr Magnetons (B.M.).**

$$\text{spin-only magnetic moment } \mu_s = \sqrt{n(n+2)}$$

Magnetic questions for our model.

Why do different complexes of the same metal ion in the same oxidation state have different numbers of unpaired electrons?

For example Fe^{3+}, Co^{3+}, and Ni^{2+}

$FeCl_3\cdot 6H_2O$ μ= 5.9 B.M.; 5 unpaired electrons	$K_3[Fe(CN)_6]$ μ= 1.7 B.M.; 1 unpaired electron
$K_3[CoF_6]$ μ= 4.9 B.M.;4 unpaired electrons	$[Co(NH_3)_6]Cl3$ μ = 0; no unpaired electrons
$[Ni(NH_3)_6]Cl_2$ μ= 2.8 B.M.; 2 unpaired electrons	$K_2[Ni(CN)_4]$ μ = 0; no unpaired electrons

Why are there only certain values of the number of unpaired electrons for a given metal ion?

For example, complexes of Fe(II) and Co(III) can only have zero or 4 unpaired electrons, never two. Complexes of Fe(III) can only have 5 unpaired electrons or 1 unpaired electron.

Why are Ni^{2+} complexes, all octahedral complexes have 2 unpaired electrons but square planar complexes are diamagnetic (no unpaired electrons)?

Coordination numbers and geometry

Why do some transition metal ions seem to have a fixed coordination number and geometry, while other metal ions seem variable?

Cr^{3+} : practically always 6-coordinate, **octahedral**

Co^{3+} : practically always 6-coordinate, **octahedral**

Co^{2+} : **both** 6-coordinate **octahedral** and 4-coordinate **tetrahedral** complexes known

Ni^{2+} : **octahedral** and **square planar** complexes common; some **tetrahedral** complexes known

Ni^{4+} : only **octahedral** complexes known

Pt^{2+} : practically always **square planar**

Reactivity

Why do some metal complexes undergo ligand-exchange reactions very rapidly and other similar complexes react very slowly, yet this reaction is thermodynamically favorable?

$$[Co(NH_3)_6]^{3+} + 6H_3O^+ \longrightarrow [Co(H_2O)_6]^{3+} + 6NH_4^+$$

The equilibrium constant for this reaction is approximately 1025, and yet an acidic solution of the hexamminecobalt(III) ion **requires several days before noticeable change occurs**.

But, the reaction of the corresponding copper(II) complex **proceeds instantaneously**.

$$[Cu(NH_3)_6]^{2+} + 6H_3O^+ \longrightarrow [Cu(H_2O)_6]^{2+} + 6NH_4^+$$

Why are the chemistries of Co^{3+}, Pt^{2+}, Cr^{3+}, and Pt^{4+} so broad with numerous examples of known, characterized, structural and geometric isomers and yet other transition metal ion chemistry is seemingly limited?

There are three isomers of $CrCl_3 \cdot 6H_2O$ that have been isolated and characterized. ($[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$).

Why is there no interconversion to the most stable compound?

Why doesn't $FeCl_3 \cdot 6H_2O$ have any isomers?

Why doesn't **cis-$[Pt(NH_3)_2Cl_2]$** convert readily to trans-$[Pt(NH_3)_2Cl_2]$?

Course Outline

I. **Introduction to Transition Metal Complexes.**

Classical complexes (Jorgenson and Werner)
Survey of ligand coordination numbers, geometries and types of ligands
Nomenclature
Isomerism

II. **Bonding in Transition Metal Complexes.**

Electron configuration of transition metals
Crystal field theory
Valence bond theory
Simple Molecular Orbital Theory
Electronic Spectra and Magnetism

III. **Kinetics and Mechanisms of Inorganic Reactions.**

Stability and lability
Substitution reactions
Electron transfer reactions

IV. **Descriptive Chemistry of TMs.**

V. **Organometallic Chemistry**

18 e^- rule, σ, and π bonding ligands (synergistic bonding)
Metal carbonyls, synthesis, structure, reactions
Compounds with delocalized π-conjugated organic ligands.
Reactions and catalysis

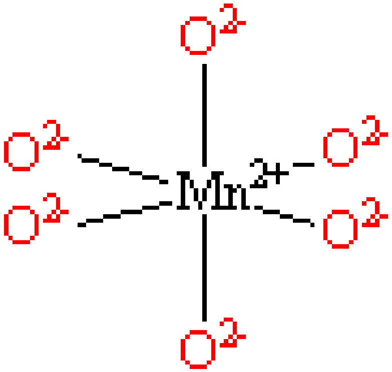
Crystal Field Theory

At roughly the same time that chemists were developing the valence-bond model for coordination complexes, physicists such as Hans Bethe, John Van Vleck, and Leslie Orgel were developing an alternative known as **crystal field theory (CFT)**.

CFT tries to describe the influence of the electrical field of neighboring ions on the energies of the valence orbitals of an ion in a crystal.

Crystal field theory was developed by considering two compounds: manganese(II) oxide, MnO **(octahedral)**, and copper(I) chloride, CuCl **(tetrahedral)**.

MnO

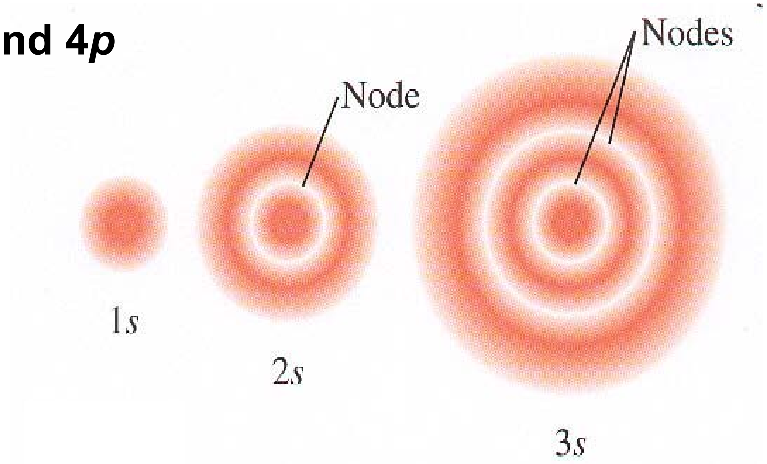


Each Mn^{2+} ion is surrounded by 6 O^{2-} in an octahedral geometry. This serves as a model for transition metal complexes with 6 ligands surrounding it.

What happens to the energies of the orbitals on an Mn^{2+} ion when this ion is buried in an MnO crystal?

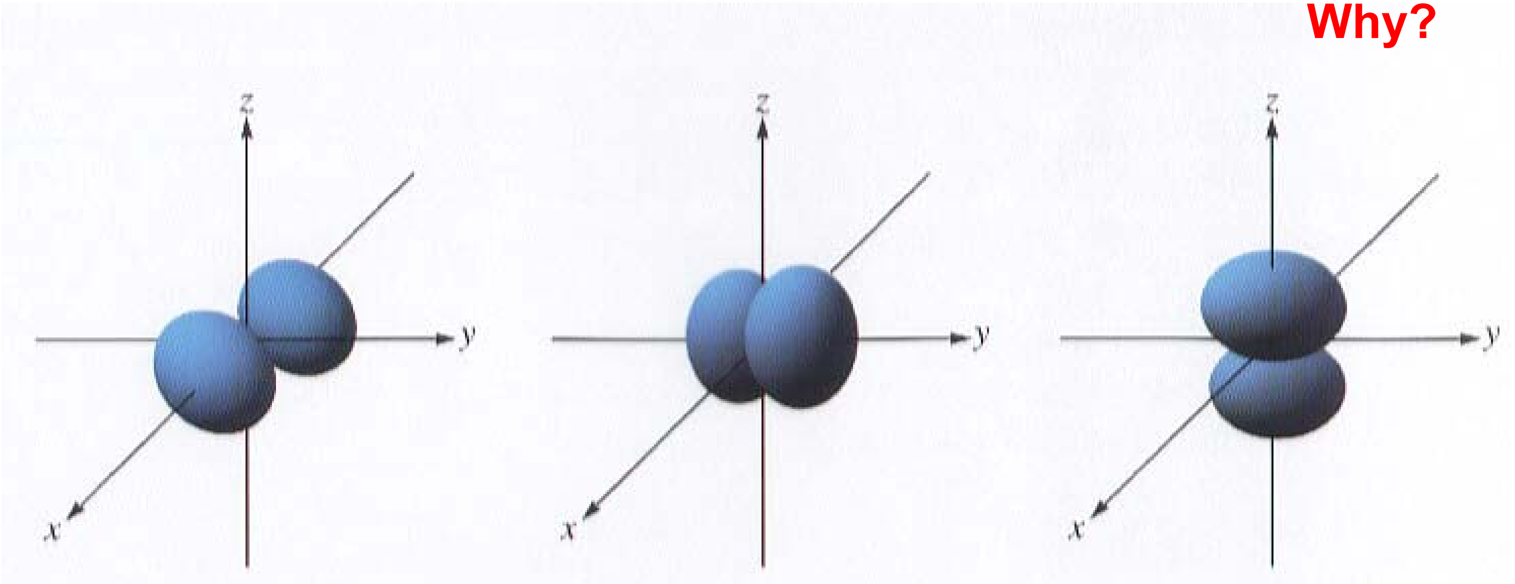
CFT cont'd

4*s* and 4*p*



Although repulsion between electrons will likely occur between electrons in these orbitals and the electrons on the six O^{2-} ions surrounding the metal ion in MnO and increase the energies of these orbitals. These orbitals will remain degenerate (have the same energy).

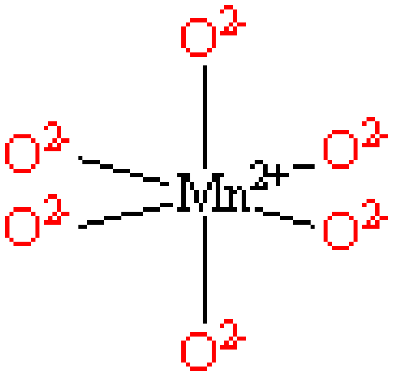
Why?

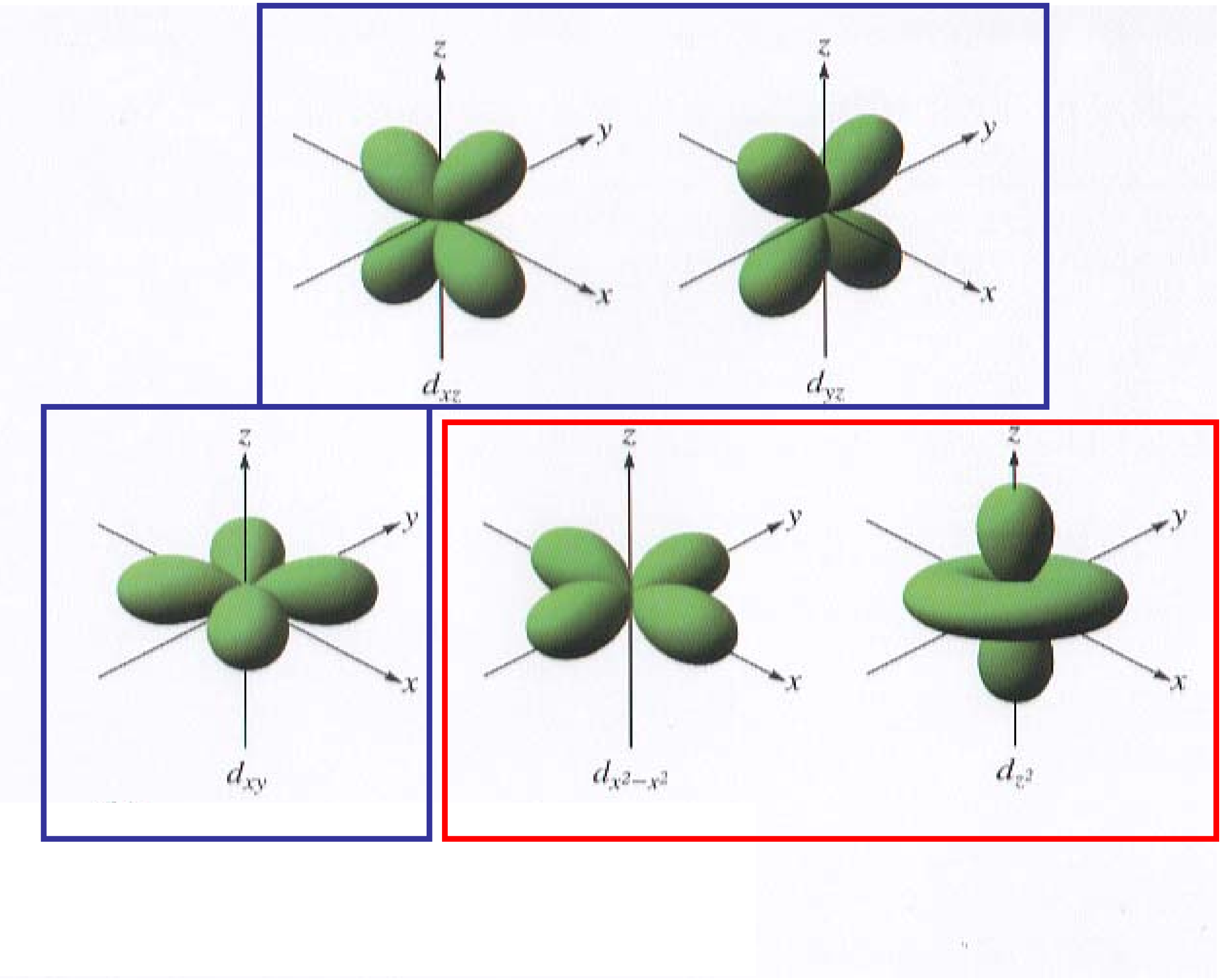


CFT cont’d

3d

What is different about the d-orbitals?





Assume the six O^{2-} ions surrounding each Mn^{2+} ion define an *XYZ* coordinate system.

Two of the 3*d* orbitals on the Mn^{2+} ion point directly toward the six O^{2-} ions

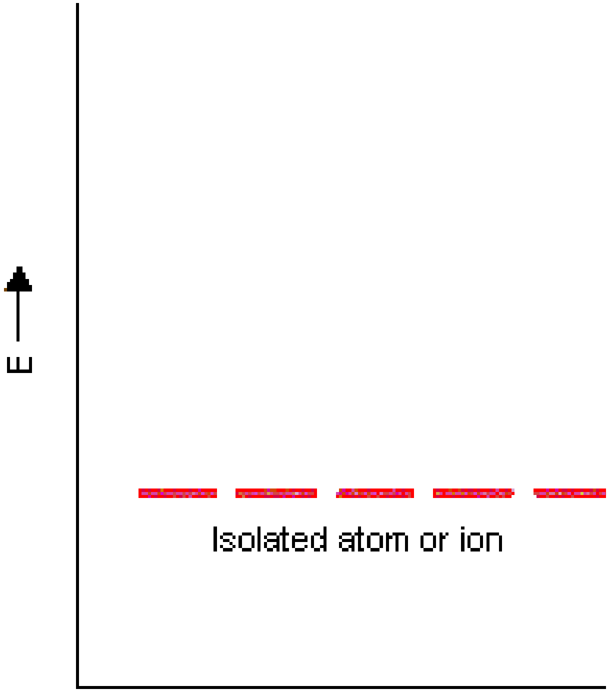
The other three orbitals lie between the O^{2-} ions

Affects on d-orbital energies

As with the energy of the 4s and 4p orbitals, the energy of the five 3*d* orbitals increases when the O^{2-} ions are brought close to the Mn^{2+} ion.

Differences arise because and the energy of the $3_{dx2\text{-}y2}$ and $3d_{z2}$ increases much more than the energy of the $3d_{xy}$, $3d_{xz}$, and $3d_{yz}$.

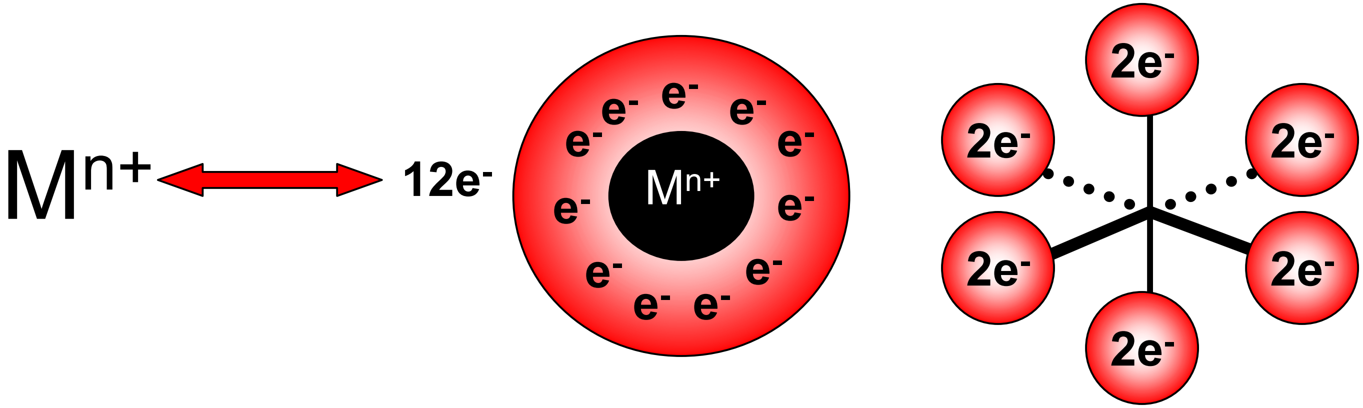
As a result of the crystal field of the six O^{2-} ions in MnO the degeneracy of the five 3*d* orbitals is split.

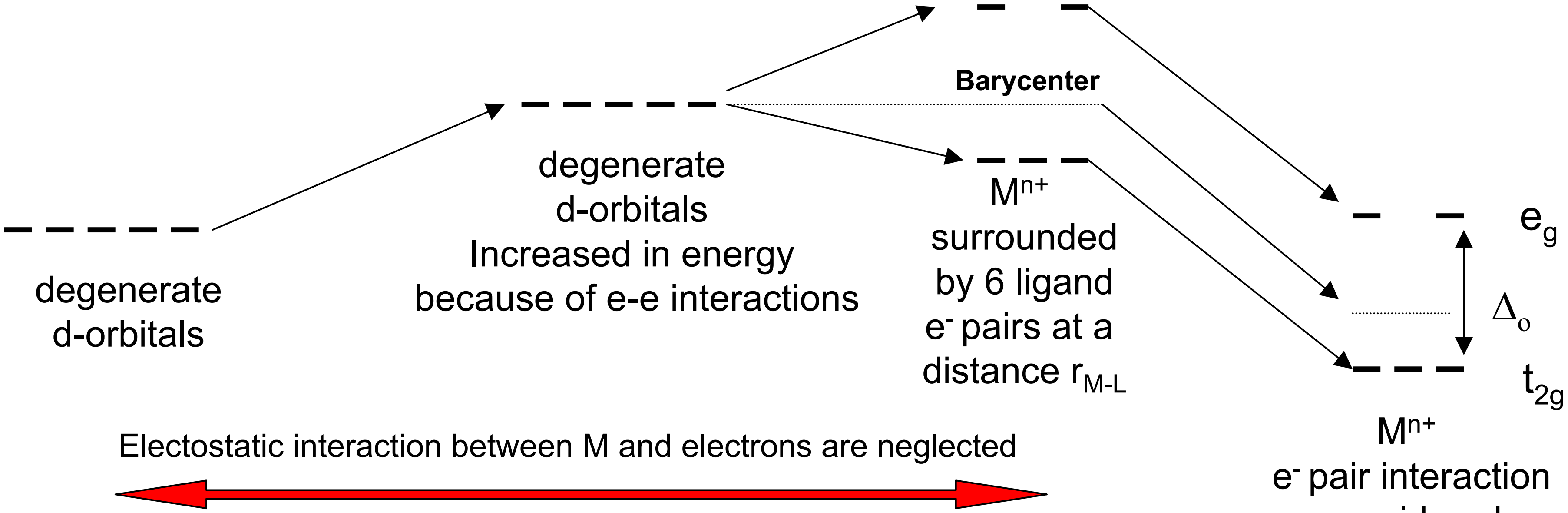


Affects on d-orbital energies

(a more general case)

Consider a general first row TM, M^{n+} with an unspecified number of d-electrons.





degenerate
d-orbitals

degenerate
d-orbitals
Increased in energy
because of e-e interactions

M^{n+}
surrounded
by 6 ligand
e^- pairs at a
distance $r_{M\text{-}L}$

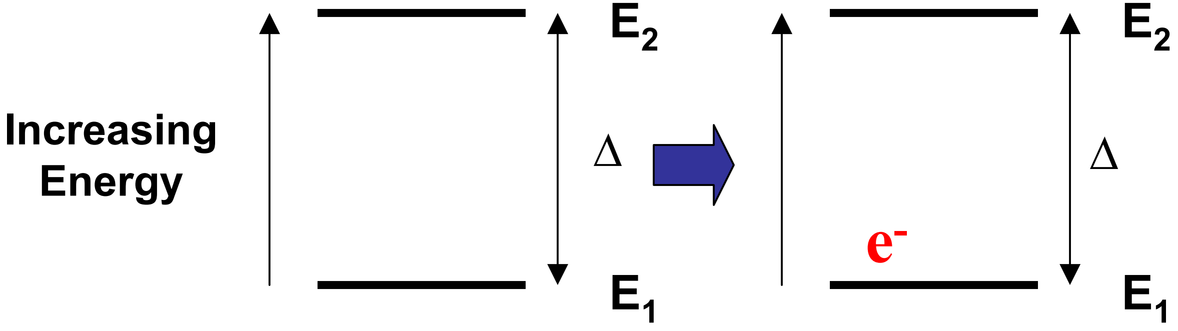
M^{n+}
e^- pair interaction
considered

Electostatic interaction between M and electrons are neglected

Crystal Field Splitting
vs.
Electron Pairing Energies

Start with two nondegenerate valence electronic energy levels.

What happens if we put 2 electrons into these orbitals?



Insert 1 electron. It goes into the lowest energy level.

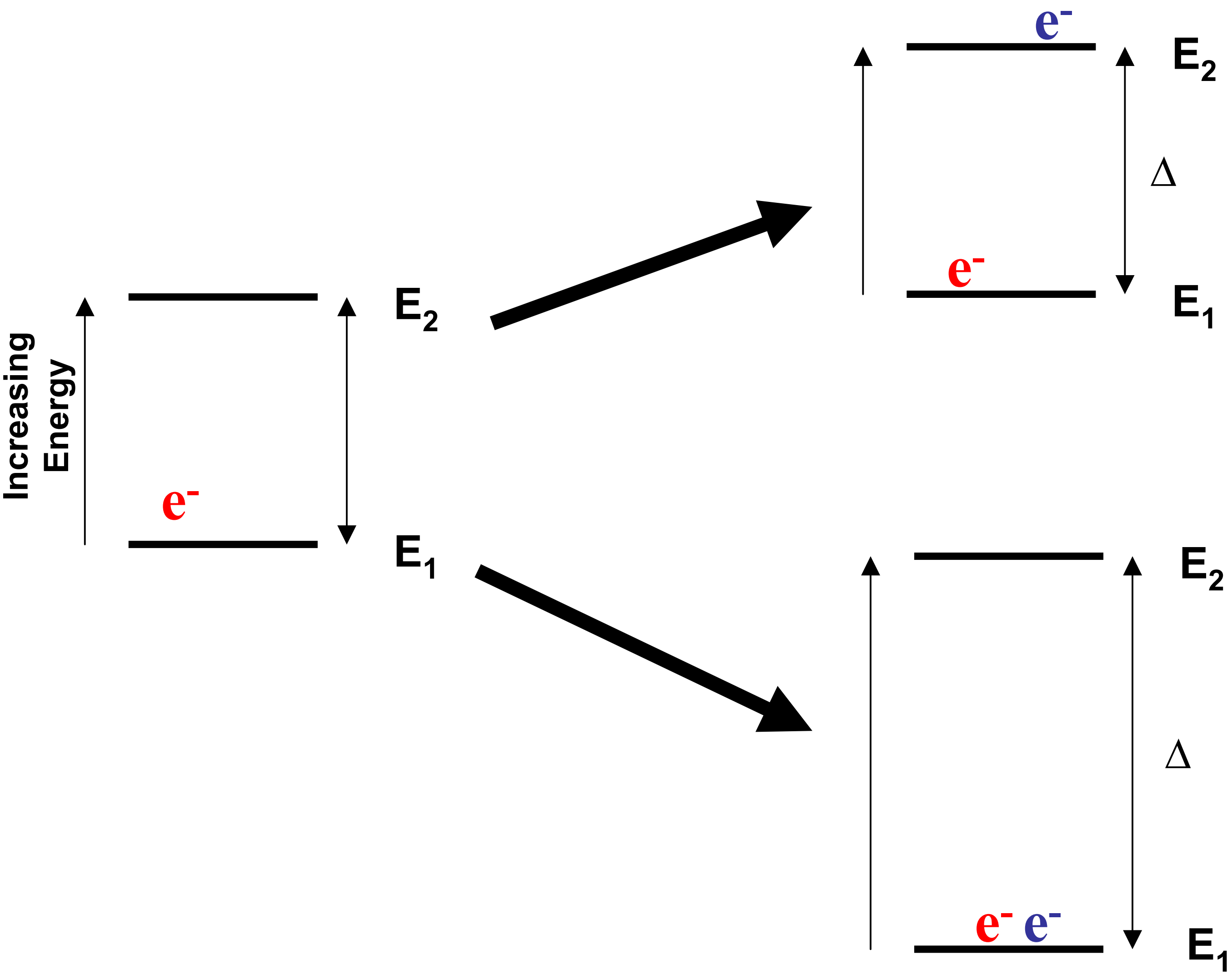
What about the second electron?

There are two cases that must be considered.

Low Spin vs. High Spin

This is similar to what you saw in 331 for filling of d-orbitals.

Energy is required to **pair electrons in the E_1** energy level.



Case II

(Weak field, high spin)

This is preferred when Δ < paring energy. The total energy for the process is $\mathbf{E_{net}=E_1+E_2}$

$\mathbf{= 2E_1 + \Delta}$.

Case I

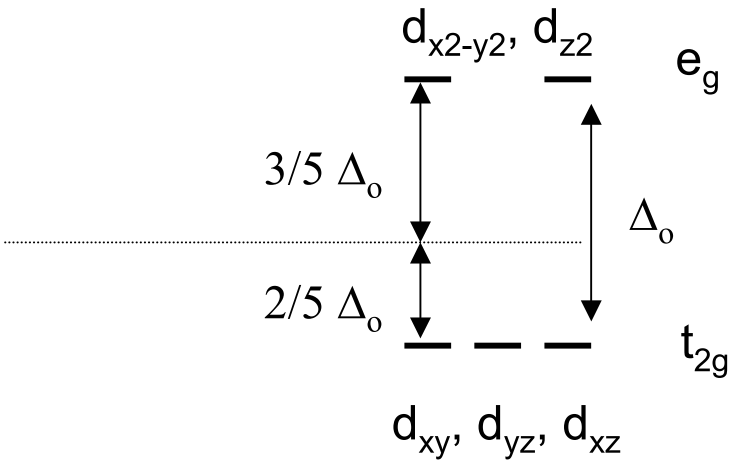
(Strong field, low spin)

This is preferred when Δ > paring energy. The total energy for the process is $\mathbf{E_{net}=2E_1+P}$.

Crystal Field Stabilization Energies

What happens when this is applied to degenerate orbitals similar to that seen for energy levels of a metal within an octahedral field?

Octahedral Geometry

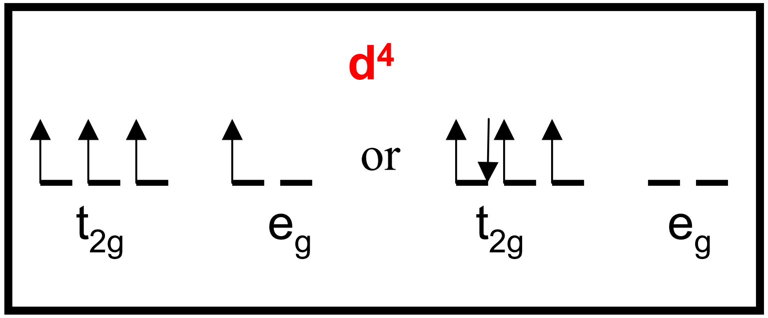


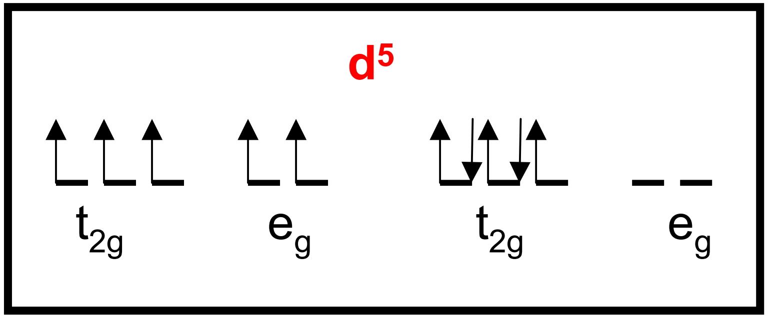
For **d^1, d^2, d^3** there is no choice where the electrons are placed.

This is also the case for **d^8, d^9, d^{10}.**

The questions arise for **d^4, d^5, d^6, d^7.**

How can we understand what configuration is assumed?





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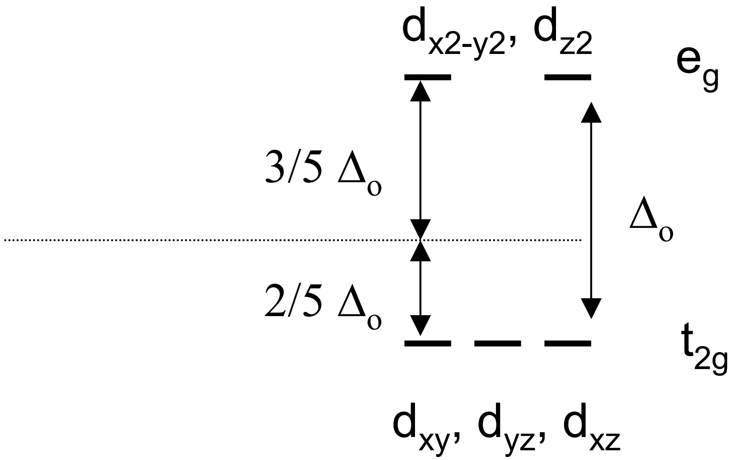
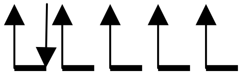
Crystal Field Stabilization Energies

How are they calculated?

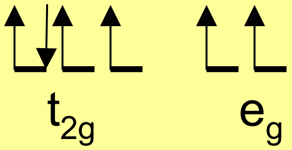


The Reference Unsplit System



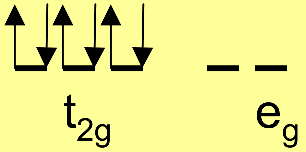
Has 1 “paired set” of electrons.

d^6-High Spin



CFSE $= 4(2/5\ \Delta_o) - 2(3/5\ \Delta_o)$
$= 2/5\ \Delta_o$

d^6-Low Spin

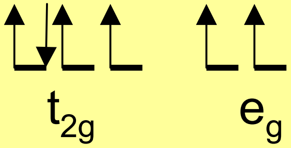


?

CFSE $= 6(2/5\ \Delta_o) - 2P$
$= 12/5\ \Delta_o - 2P$

Which configuration will occur?

d^6-High Spin

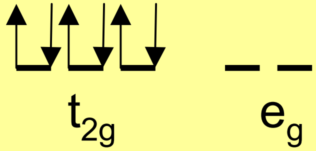


CFSE $= 4(2/5\ \Delta_o) - 2(3/5\ \Delta_o)$

$= 2/5\ \Delta_o$

$= 12/5\ \Delta_o - 2\Delta_o$

d^6-Low Spin



CFSE $= 6(2/5\ \Delta_o) - 2P$

$= 12/5\ \Delta_o - 2P$

The difference between the energy of the two configurations is relative to the differences between Δ_o and **P**.

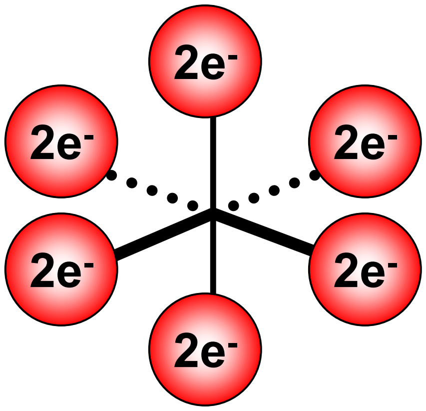
Hence,

If $\Delta_o > P$ the **low-spin** case has greater CFT stabilization energy.

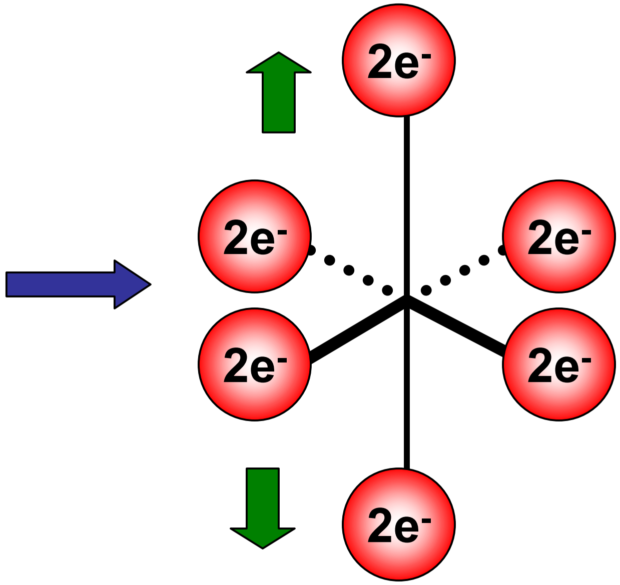
If $\Delta_o < P$ the **high-spin** case has greater CFT stabilization energy.

Similar results are seen in similar analysis of **d^4, d^5, and d^7.**

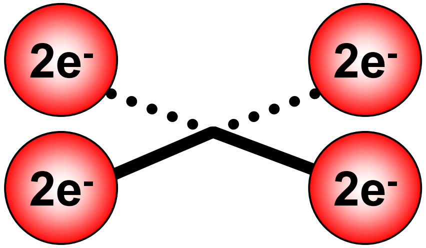
Tetragonal Octahedral and Square Planar Fields



Octahedral field

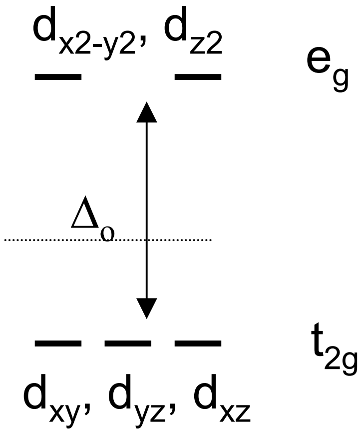


Tetragonally elongated octahedral field

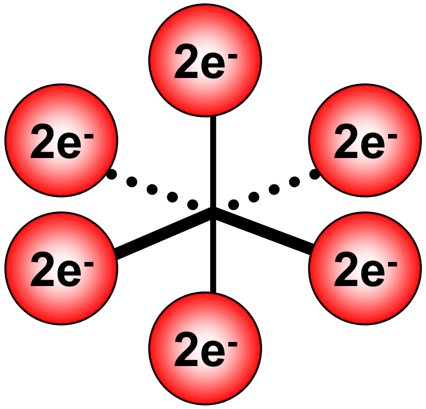


Square planar field

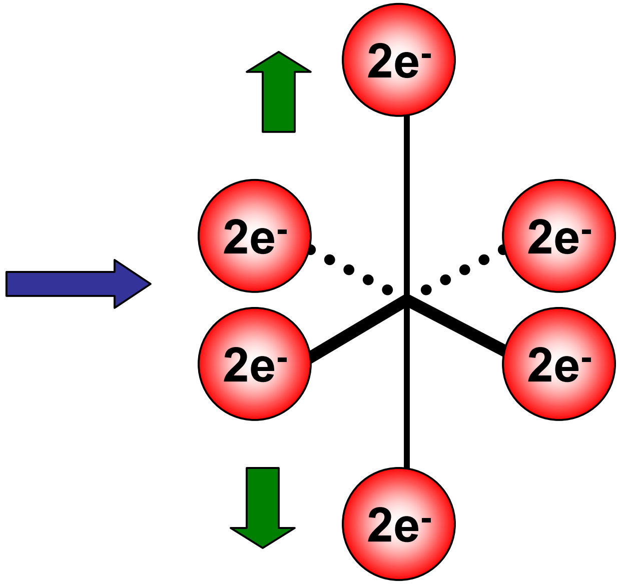
Try Assignment #2 Question #6



Tetragonally Distorted Field

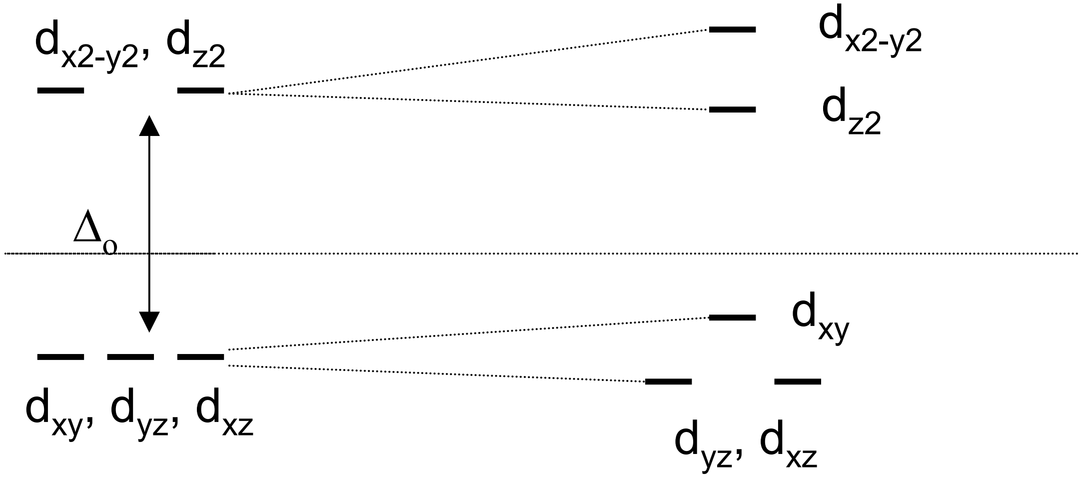


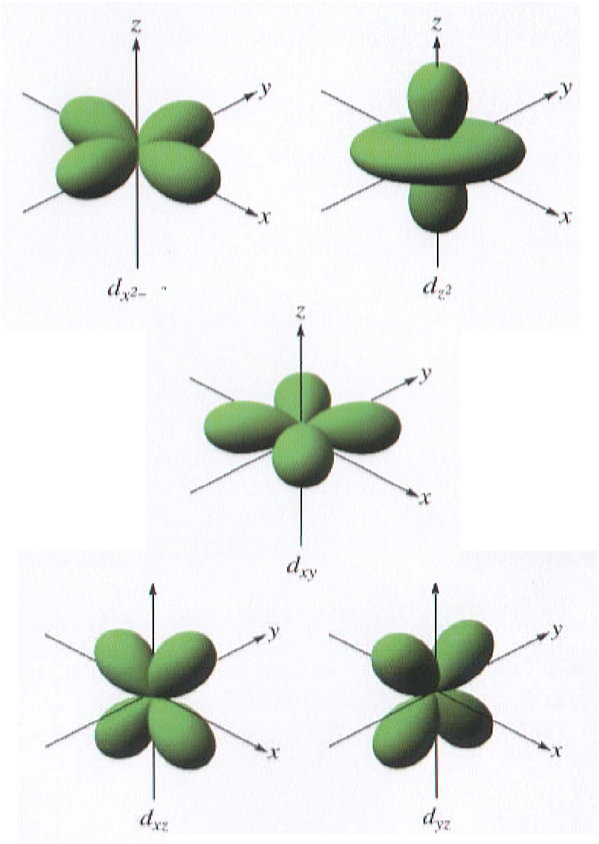
Octahedral field



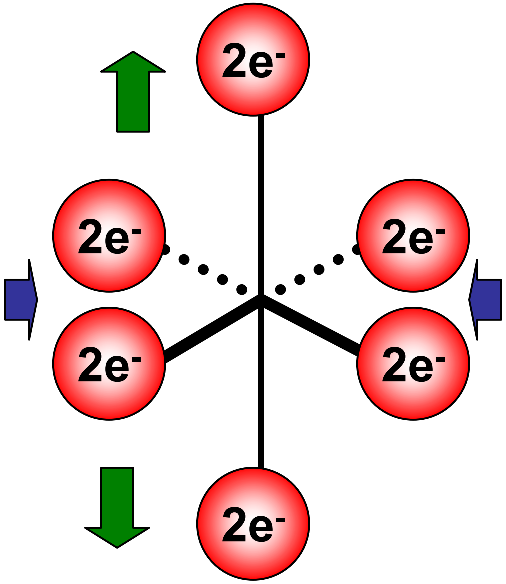
Tetragonally elongated octahedral field

elongation in the z-direction





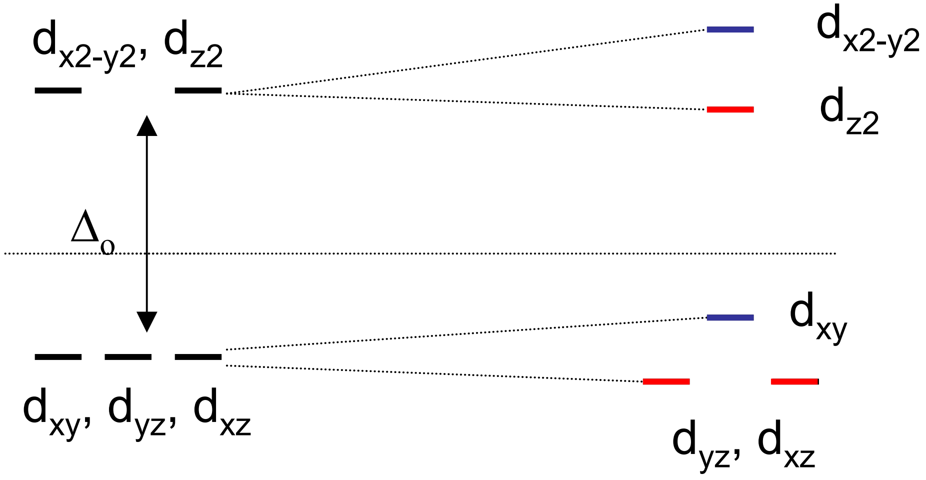
Understanding the energy changes for the tetragonal distortion



When elongation occurs in the z-direction, simultaneous contraction in the x- and y-direction results from the availability of space around M^{n+}.

The coulombic attraction between the ligan electrons and the charge of the metal center pulls the ligand closer.

What about orbital energy changes?



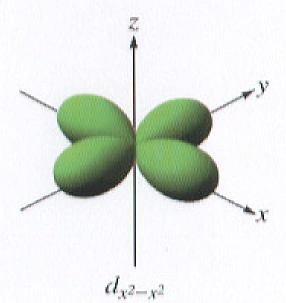
The barycenter remains constant.

Orbitals with a “z” component become more stable.

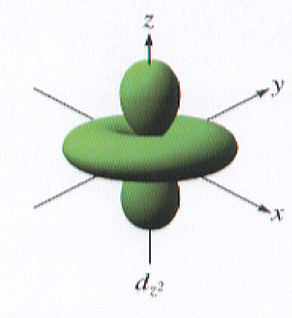
Why?…..it’s electrostatics.

Orbitals with “ x and y” components become less stable.

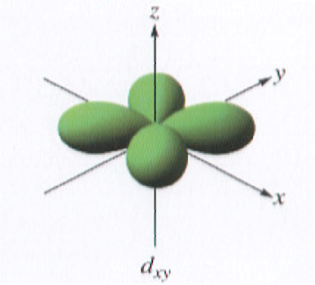
A summary of the effects on the orbital energies.



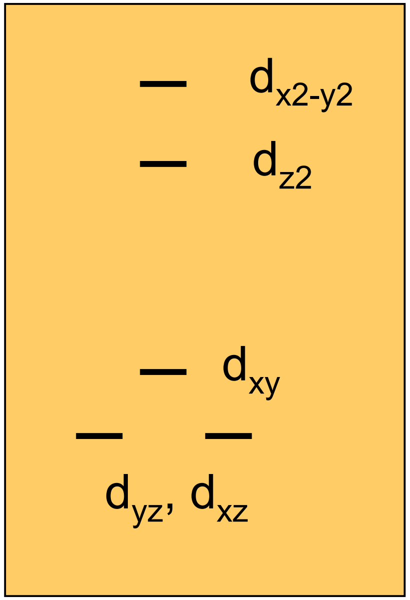
The d_{x2-y2} orbital is increased in energy because it is directed toward the x- and y- ligands which have approached the M center more closely.



The d_{z2} orbital is decreased in energy because it is directed toward the retreating z- ligands. The change in energy of the d_{z2} orbital is greater than the d_{yz} and d_{xz} because it is directed the elongated positions.



The d_{xy} orbital is increased in energy because it is directed toward the x- and y- ligands which have approached the M center more closely. This results in more e-e repulsion between e in the d-orbital and on the ligands.

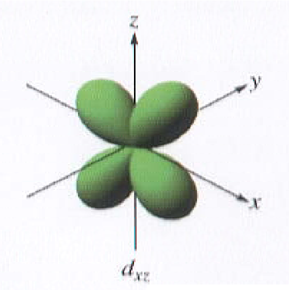


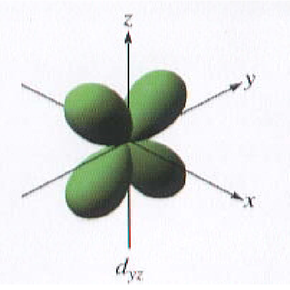
d_{x2-y2}

d_{z2}

d_{xy}

d_{yz}, d_{xz}





The d_{yz} and d_{xz} orbitals are decreased in energy because they feel direct influence of the retreating z- ligands. The change in energy of the d_{z2} orbitals is greater than that seen for the d_{yz} and d_{xz} orbitals because it is directed at the elongated positions.

Square Planar Field.

Question #6 on Assignment #2 deals with the Square planar field.

It is YOUR responsibility to apply the approach we have to this system.

A couple of important things to note:

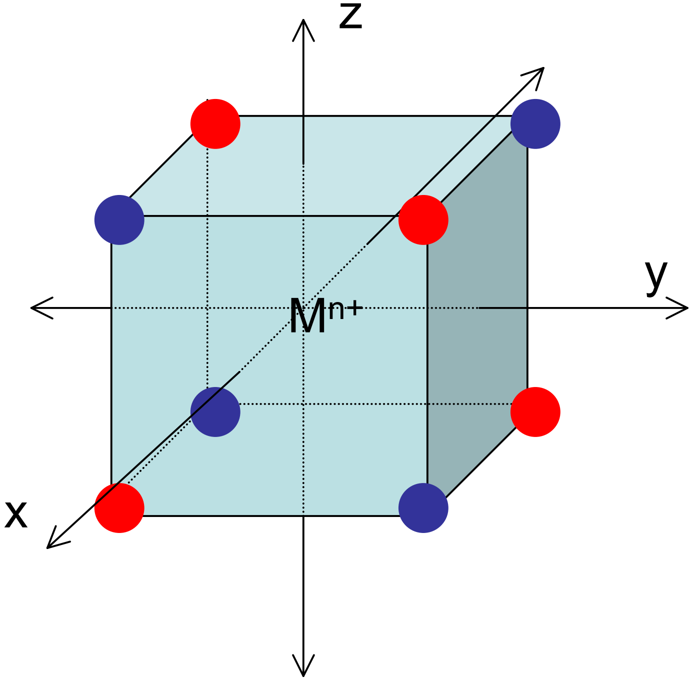
The square planar geometry is an octahedral field with NO z-ligands.

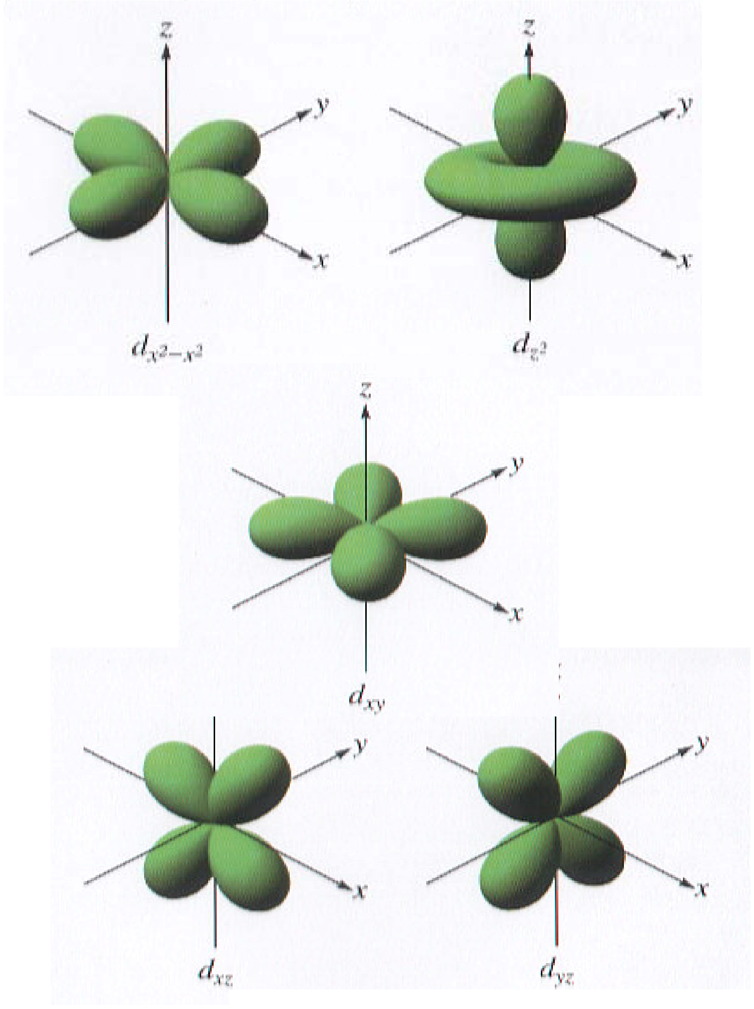
You cannot assume the Barycenter is constant. Why might this be?

Significant stabilization of metal orbitals with z components occurs.

Good Luck!

Tetrahedral Field.

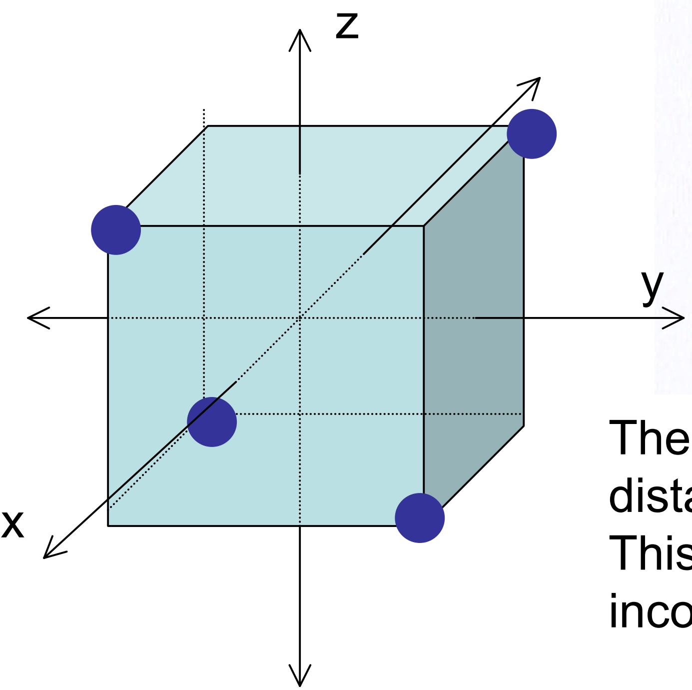


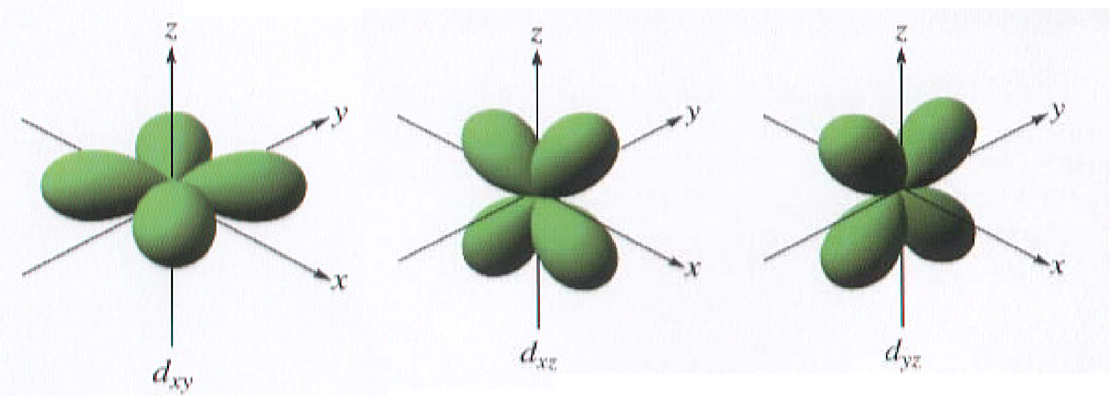


It is difficult to visualize the tetrahedral field and the d-orbitals together.

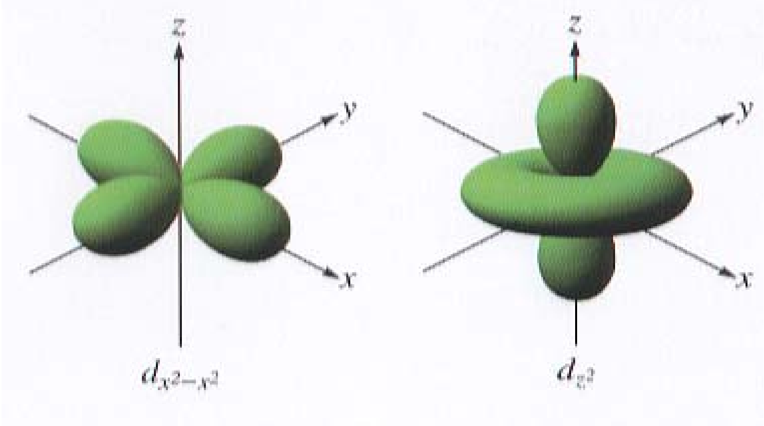
The tetrahedral field can be viewed as ligands at vertices of a cube.

Tetrahedral field and d-orbitals





The key to understanding the orbital ordering is the distance the d-orbitals are from the approaching ligands. This is because none of the d-orbitals point directly at the incoming ligands.



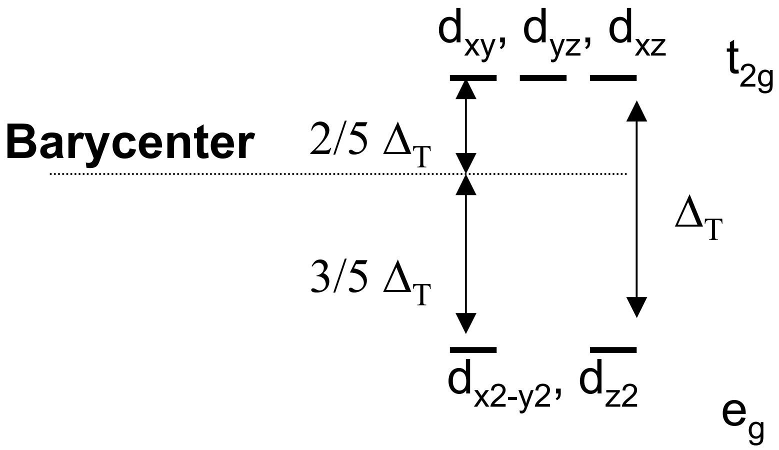
It is useful to to relate the distance of the tip of the d-orbitals from the incoming ligands in terms of the edge dimension **(L)** of the cube.

The d_{xy}, d_{yz}, and d_{xz} orbitals are **L/2** away from the ligands whereas d_{x2-y2} and d_{z2} are **L√2/2** away.

Orbital ordering in a tetrahedral field

The d_{xy}, d_{yz}, and d_{xz} orbitals are **L/2** away from the ligands whereas d_{x2-y2} and d_{z2} are **L√2/2** away.

The closer the orbitals are to the ligands the greater the interaction…and greater the increase in energy.



d_{xy}, d_{yz}, d_{xz}

t_{2g}

Barycenter

$2/5\ \Delta_T$

Δ_T

$3/5\ \Delta_T$

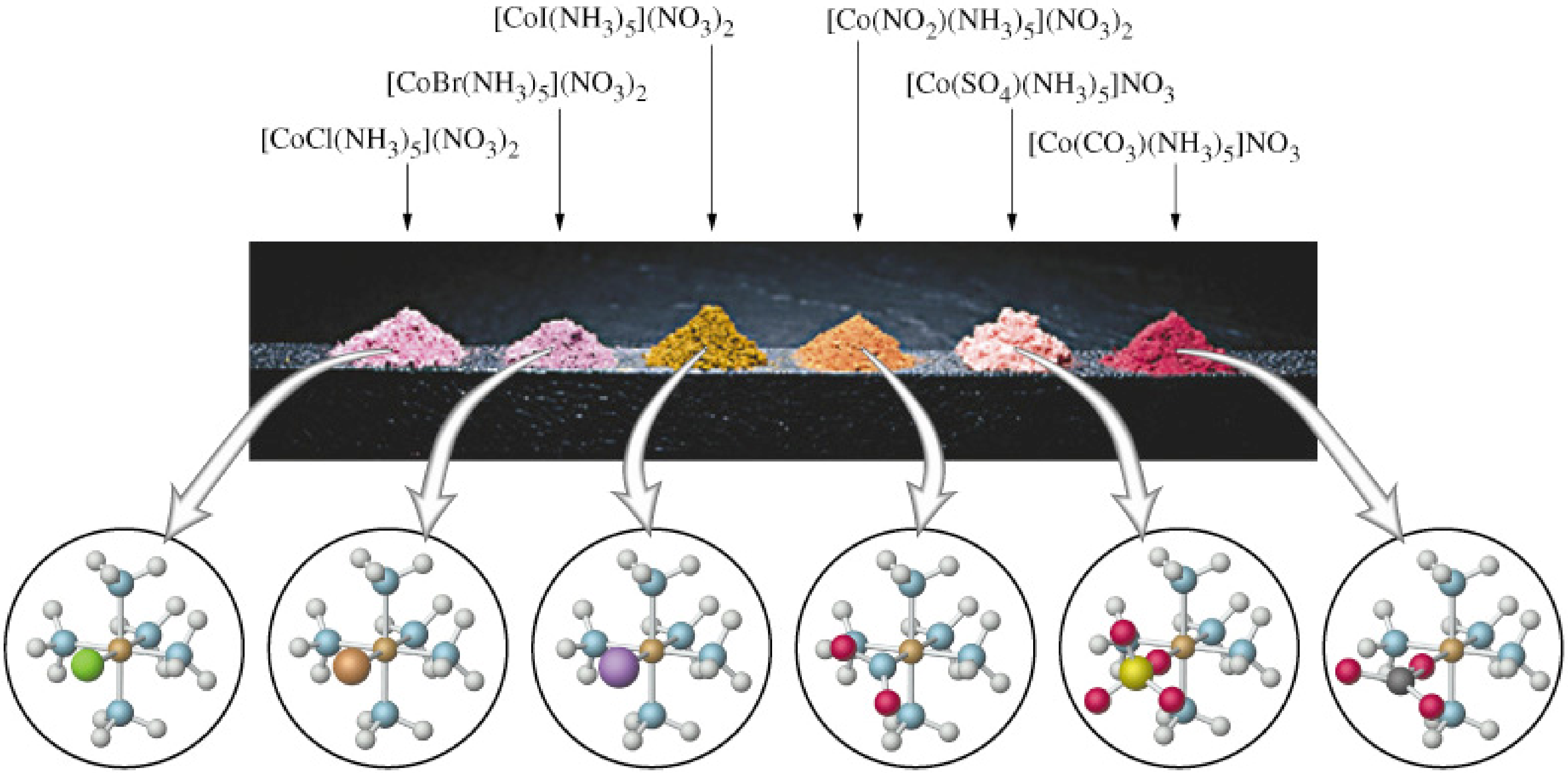
d_{x2-y2}, d_{z2}

e_g

A useful point to remember is, because of the LESS CLEAR-CUT distinction between orbital interactions the splitting of the d-orbitals in a tetrahedral field is about half that observed for an octahedral field.

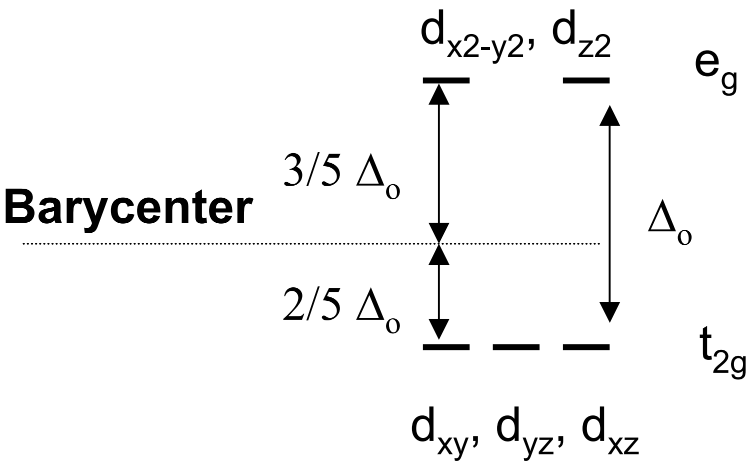
TMs and Colour:

Electronic Absorption Spectroscopy.



Where does the colour come from?

Sources of Colour in TM Complexes



d_{x2-y2}, d_{z2} e_g

Barycenter

$3/5\ \Delta_o$

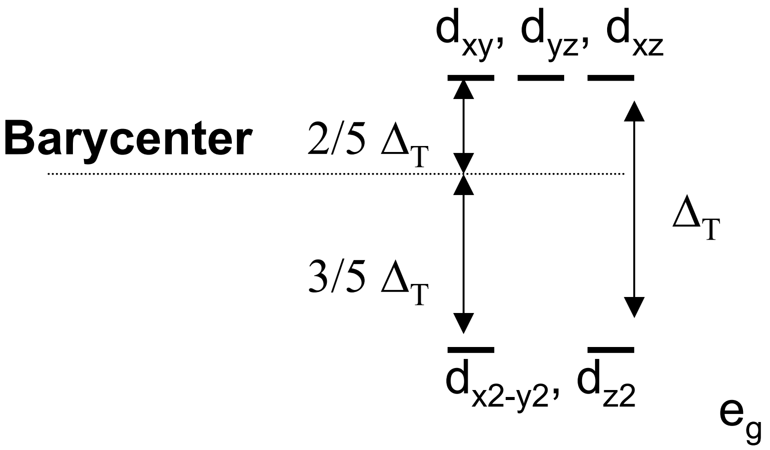
Δ_o

$2/5\ \Delta_o$

t_{2g}

d_{xy}, d_{yz}, d_{xz}

Octahedral Geometry



d_{xy}, d_{yz}, d_{xz}

Barycenter $2/5\ \Delta_T$

Δ_T

$3/5\ \Delta_T$

d_{x2-y2}, d_{z2} e_g

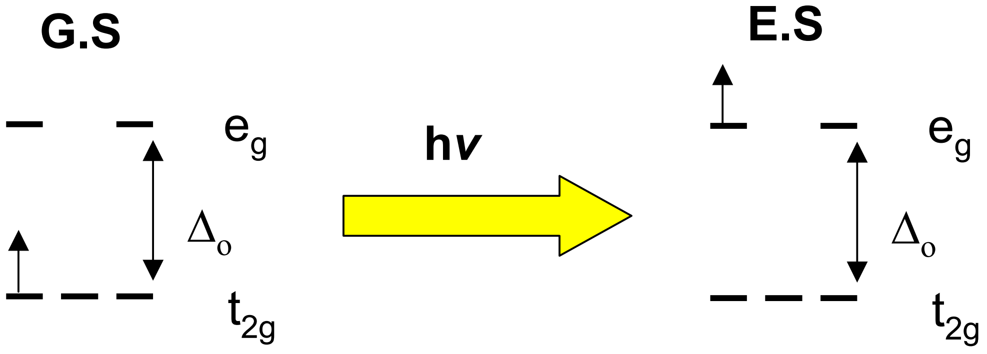
Tetrahedral Geometry

The colours of TM complexes arise from the absorption of light.

This absorption of light results in d ⇒ d transitions. (movement of the electrons)

For $[Ti(OH_2)]^{3+}$

$d^?$



G.S **E.S**

e_g Δ_o t_{2g}

h*v*

e_g Δ_o t_{2g}

$\Delta_o = hv$

$= 20\,300\ cm^{-1}$

$= 493\ nm$

$= 243\ kJ/mol$

Aspects of Colour

The *Type* of Colour.

This depends on the position of the absorption band(s); this is a fancy way to say the difference in the energy of the d-orbitals.

The *INTENSITY* of Colour.

This depends on how strongly (or weakly) the light is absorbed. This is outlined by Beer's Law. ($\in$ = the absorption coefficient; A= $\in$cl)

i) d $\Rightarrow$ d transitions are formally forbidden….. Why?

Yet the still occur but they are not intense absorptions.

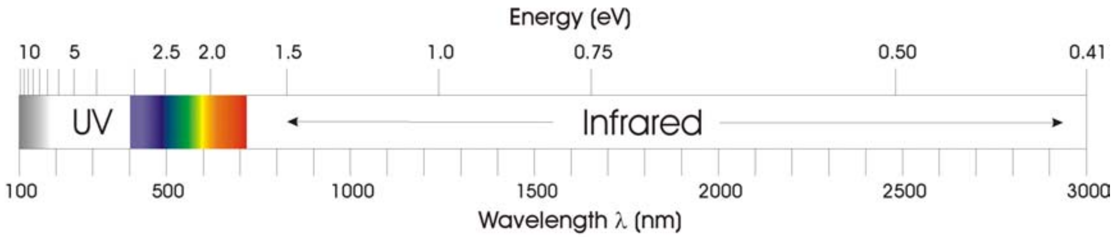
d $\Rightarrow$ d bands when molecules don't have a center of symmetry tend to be stronger.

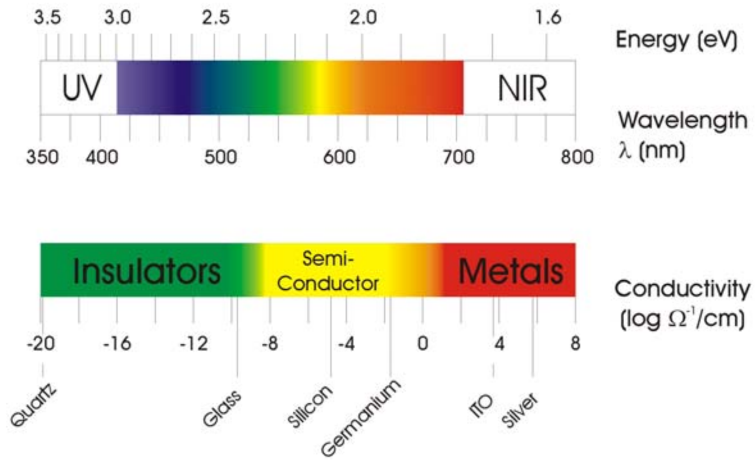
$$\in_{\mathrm{ML4(tet)}} > \in_{\mathrm{ML6(oct)}}$$

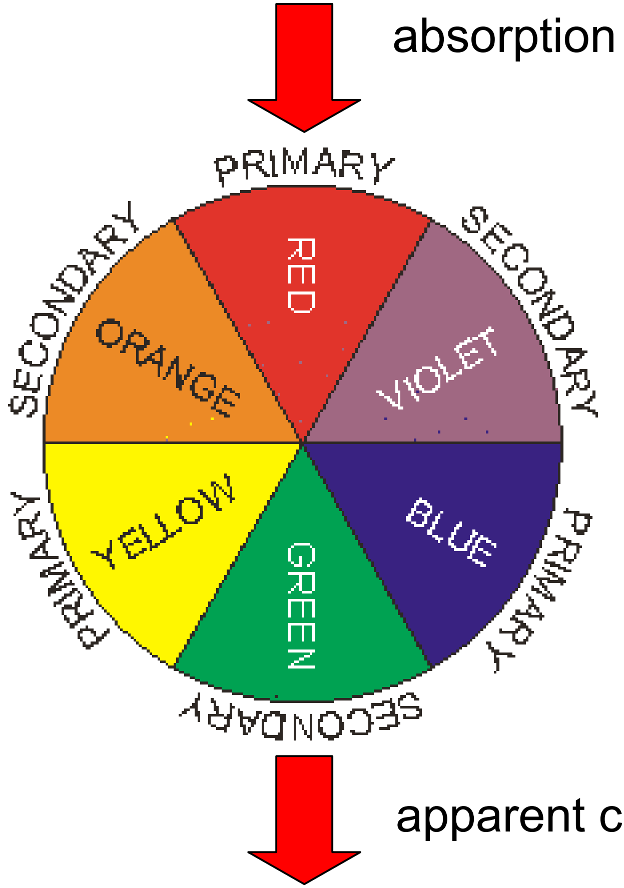
ii) Any transition that involves the change of the d-electron spin is forbidden. We often speak of "spin-allowed" and "spin-forbidden" transitions.

Light …. IT'S ENERGY!

The Electromagnetic Spectrum.







absorption

apparent colour

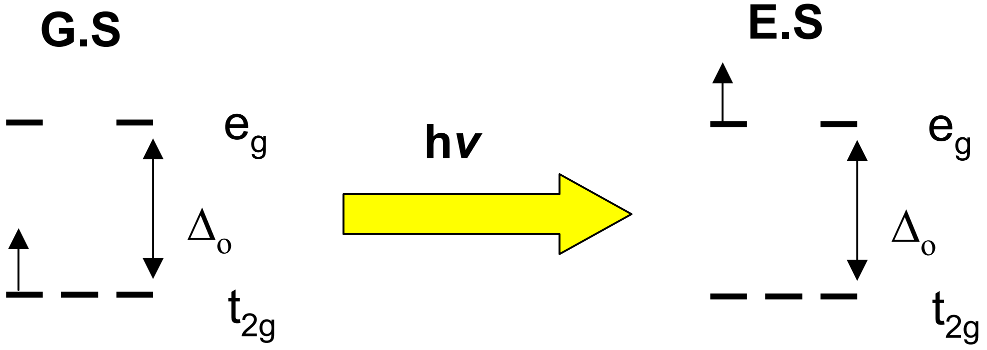
The Artists Colour Wheel.

We can determine the colour of a compound from the light it absorbs. Complimentary colours are on opposite sides of the wheel.

How many transitions?

For $[Ti(OH_2)]^{3+}$

d^1



$$\Delta_o = h\nu$$
$$= 20\,300\ cm^{-1}$$
$$= 493\ nm$$
$$= 243\ kJ/mol$$

$$t_{2g}^{1} \longrightarrow e_g^{1}$$

The absorption of visible light promotes the t_{2g} electron to the e_g.

The energy of the light corresponds to Δ_o. This is because there is only one possible transition.

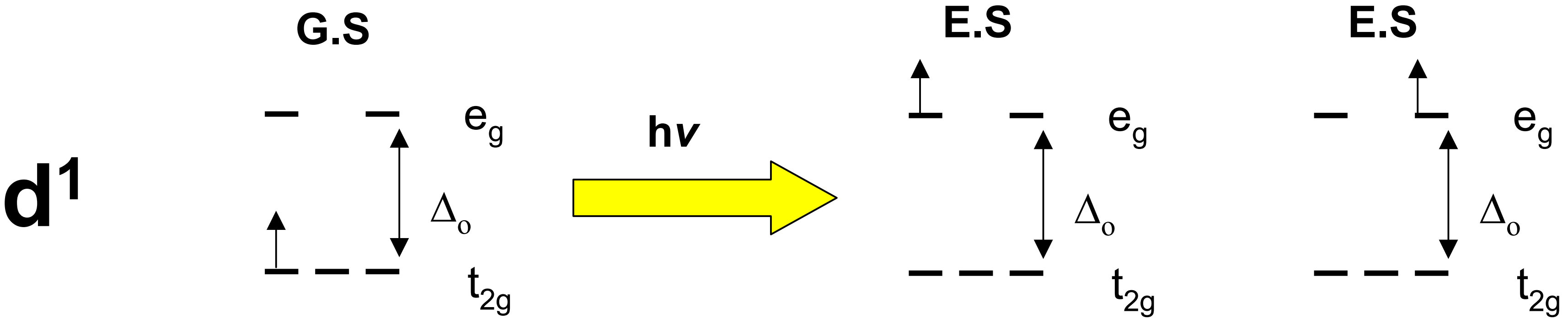
Do we see only ONE absorption if we have ONE d-electron?

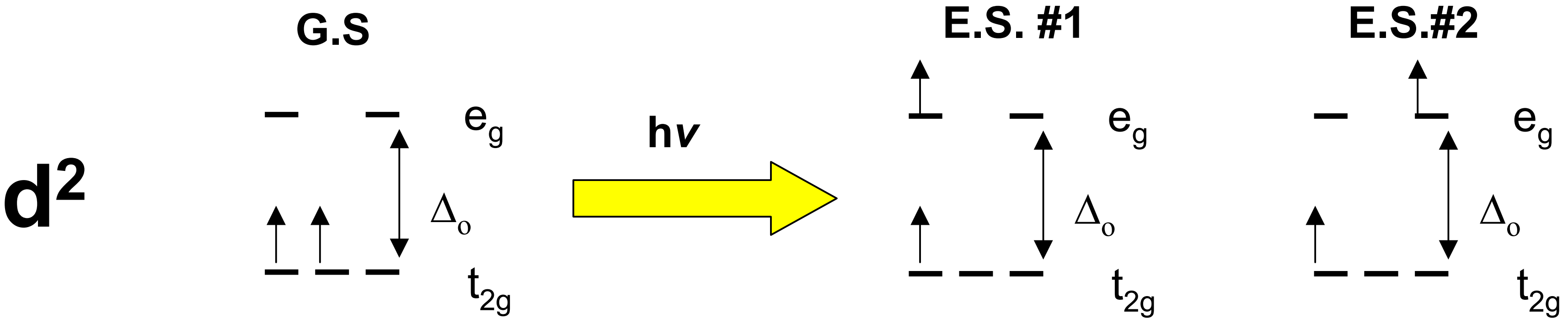
At first glance this may appear true….but is it?

d^n Transitions

We must remember that any **d ⇒ d transitions** observed are “spin-allowed”.

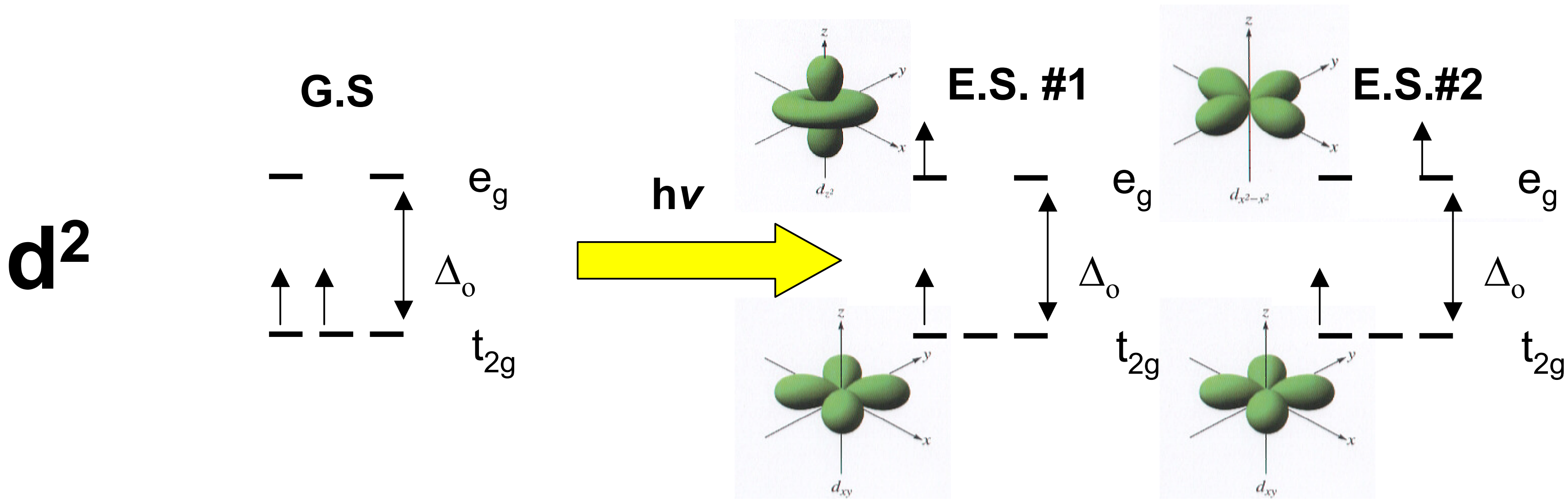
This means that in such a d^n configuration you will observe as many E.S.s as is possible as long as the spin of the electron doesn’t change.





E.S.#1 is of lower energy than E.S.#2

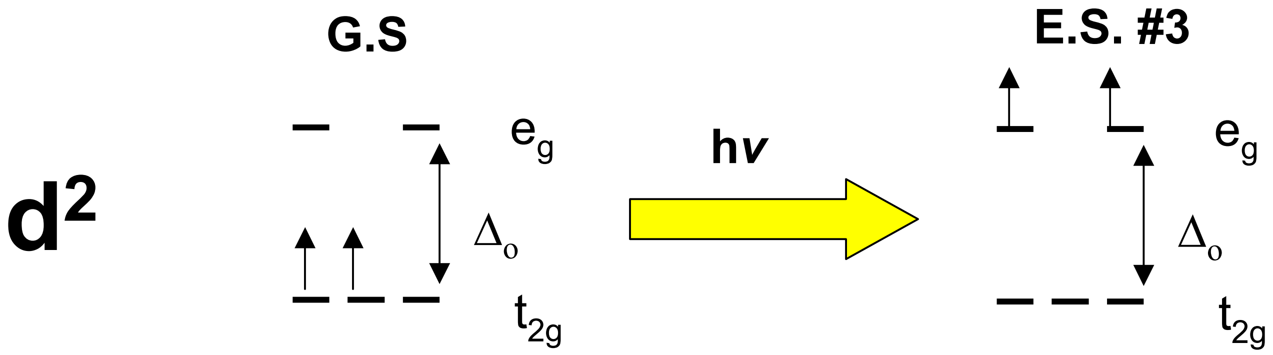
Energies of Transitions.



E.S.#1 is of lower energy than E.S.#2

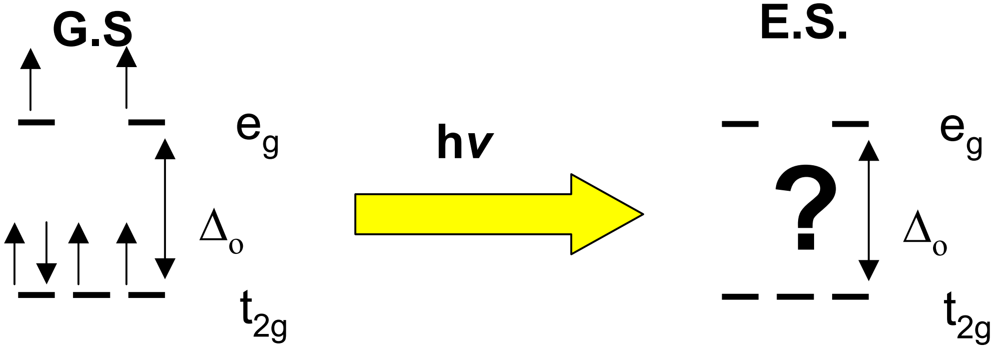
But there are three absorptions!!! WHY?

The highest energy transition corresponds to the promotion of both electrons.



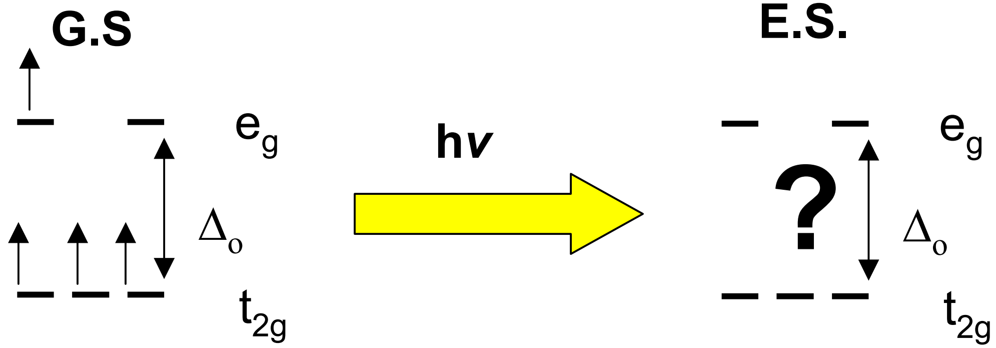
What about other d^n systems?

HS d^6 OCT

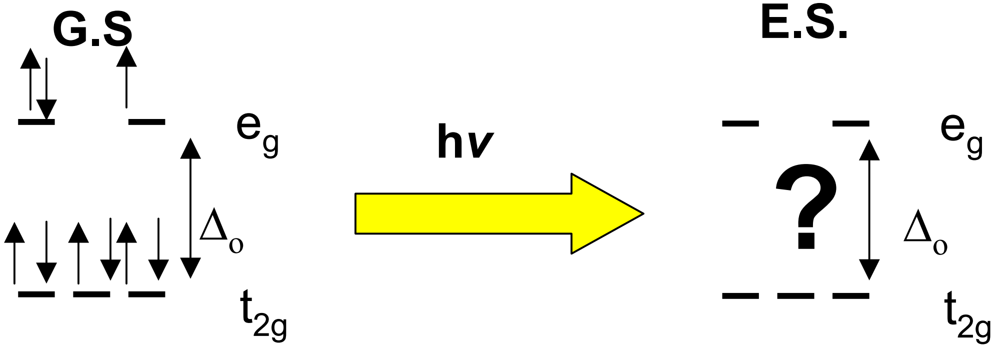


Should we see one or two transitions?

HS d^4 OCT



d^9 OCT



What governs the magnitude of Δ?

1. **The identity of the metal.**
   CFS of 2nd row TMs is ~50% greater than 1st row.
   CFS of 3rd row TMs is ~25% greater than 2nd row.

There is also a small increase in CFS along each period.

2. **The Oxidation State of the metal.**

   Generally, the higher the oxidation state of the metal the greater the splitting. This explains why Co(II) complexes are H.S. and most Co (III) complexes are L.S.

3. **The Number of Ligands.**

   This was already hinted at when we looked at Tetrahedral vs. Octahedral splitting. In this case the $\Delta_T \sim 4/9\ \Delta_O$.

4. **The nature of the ligands.**

Invisible Ink

$$2[Co(H_2O)_6]Cl_{2(s)} \xrightarrow{\textbf{heat}} Co[CoCl_4]_{(s)} + 12\ H_2O$$

Why does this happen?

Spectrochemical Series

The splitting of *d* orbitals in the crystal field model not only depends on the **geometry** of the complex, it also depends on the **nature of the metal ion**, the **charge on this ion**, and the **ligands** that surround the metal.

When the geometry and the ligands remain constant, splitting decreases in the following order:

$$Pt^{4+} > Ir^{3+} > Rh^{3+} > Co^{3+} > Cr^{3+} > Fe^{3+} > Fe^{2+} > Co^{2+} > Ni^{2+} > Mn^{2+}$$

strong-field ions ... weak-field ions

When the geometry and the metal are held constant, splitting of the *d* orbitals decreases in the following order:

$$CO \sim CN^- > NO_2^- > NH_3 > \textbf{-}NCS^- > H_2O > OH^- > F^- > \textbf{-}SCN^- \sim Cl^- > Br^-$$

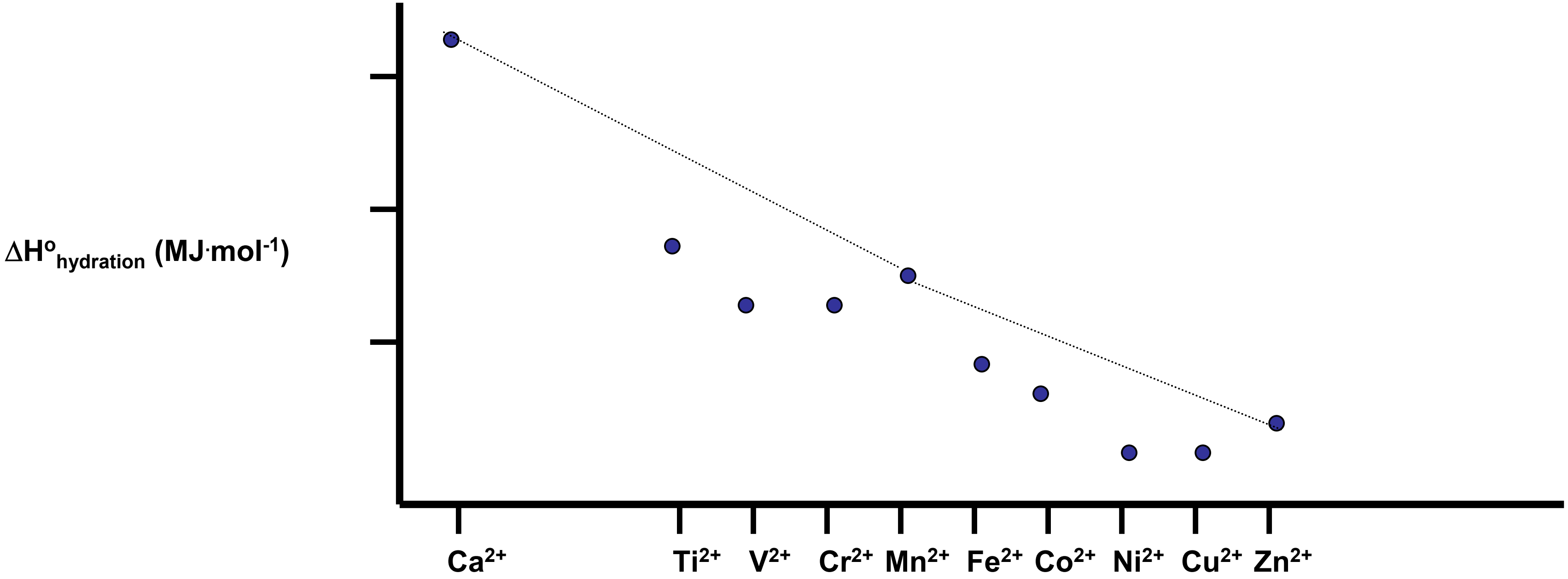
strong-field ligands ... weak-field ligands

Hydration Enthalpies

A success of CFT.

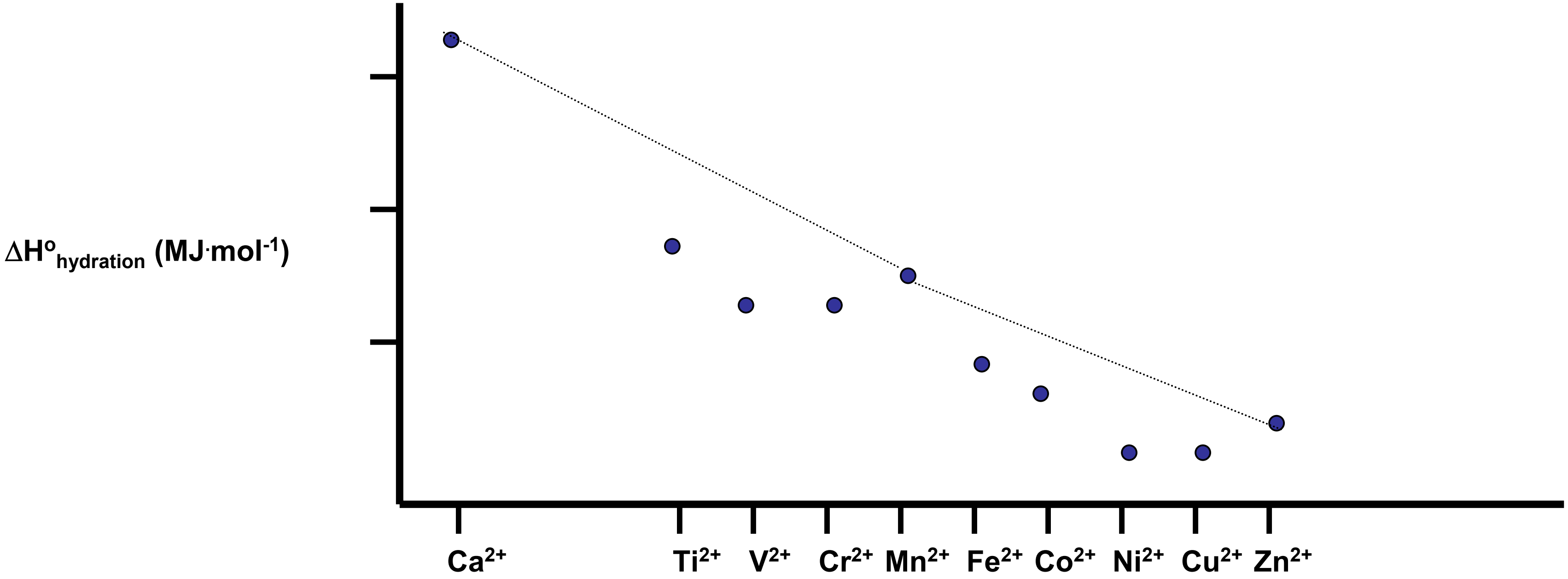
$$\mathbf{M^{n+}_{(g)} + 6H_2O_{(l)} \longrightarrow [M(OH_2)_6]^{n+}_{(aq)}}$$

What do you expect?
What would you use to predict the trend across the period?

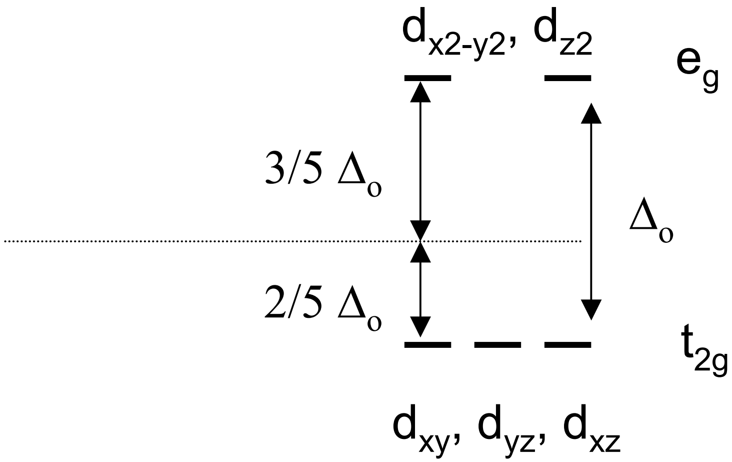


How can we use CFT to understand this?

CFT and Hydration Enthalpies



The more exothermic hydration enthalpy is the result of the CFSE which may be determined as a fraction of Δ.



The only exceptions are d^0, d^5 H.S. and d^{10}.
WHY?

NOTE. On p.438 of R.C. all stabilization energies are noted as negative.
THIS IS NOT CORRECT!

Do similar observations appear elsewhere?

Lattice energies of MCl_2.

MX interatomic distances for transition metal halides.

Ionic radii for divalent TM cations. (3d series)

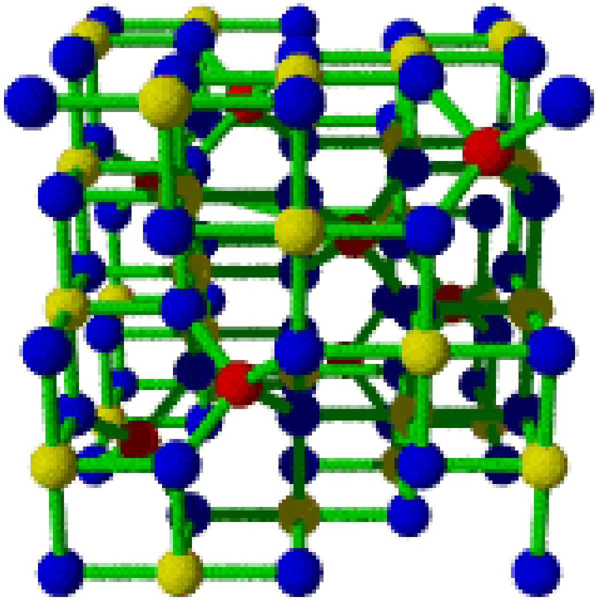
The same explanation used for hydration energies can be applied to these systems.

Spinel Structures.

CFT aids in understanding the arrangements of metal ions in spinel structures (R.C. Chpt.12).

READ RODGERS WHERE SPINEL STRUCTURES ARE OUTLINED IN DETAIL. (p. 182-185).

The spinel is a **MIXED METAL OXIDE** with a general formula $(M^{2+})(2M^{3+})(O^{2-})_4$..



Spinel is $MgAl_2O_4$

Many compounds adopt this type of structure.

The basic structure is a FCC lattice of O^{2-} anions.

Cations occupy tetrahedral and octahedral holes.

How does CFT help us understand this structure?

Spinel structures and CFT

Normal Spinal Structure.

M^{2+} is tetrahedral, M^{3+} is octahedral   Example: $(Mg^{2+})_T(2Al^{3+})_O(O^{2-})_4$

Inverse Spinal Structure.

M^{2+} is octahedral M^{3+} is tetrahedral and in the remaining octahedral holes
Example: $(Fe^{3+})_T(Fe^{2+},Fe^{3+})_O(O^{2-})_4$

This later example is magnetite or Fe_3O_4.

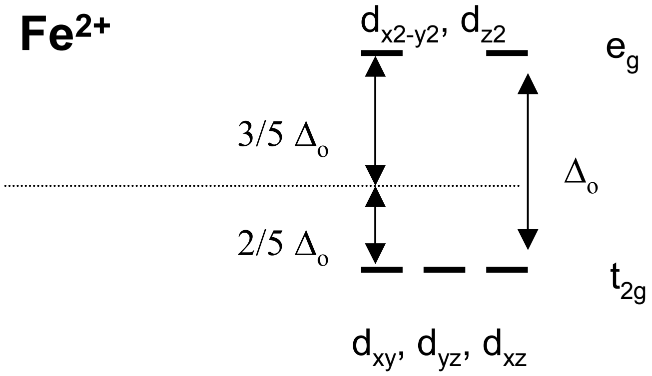
Fe_3O_4 $(Fe^{2+}, 2Fe^{3+}, 2O^{2-})$

Note the O^{2-} is a weak field ligand. (Fe is H.S.)

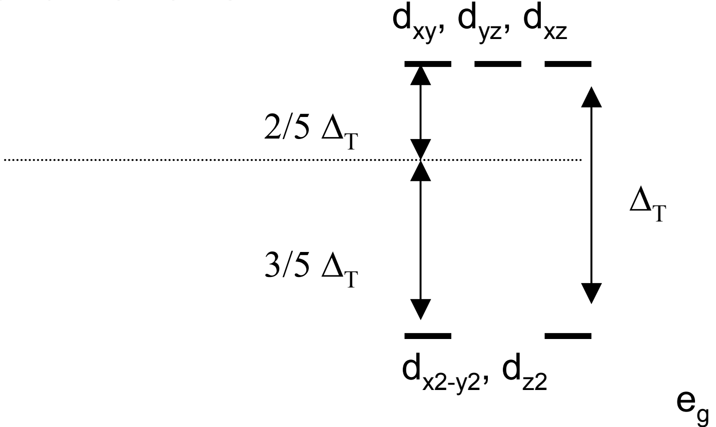
Fe^0 is d^8

What are the electron configurations of the Fe ions?

Fe^{2+}



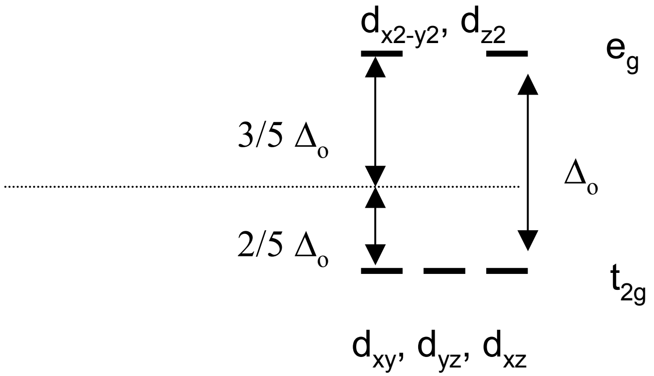
OR



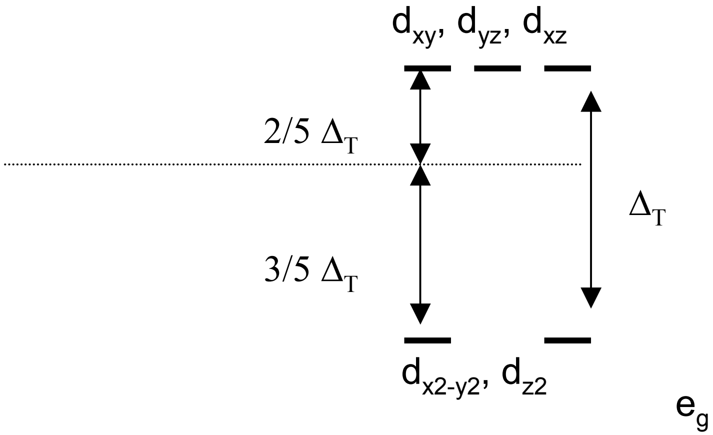
Mn_3O_4 Spinel Structure.

Mn_3O_4 (Mn^{2+}, $2Mn^{3+}$, $4O^{2-}$)

Electron configurations are ….. ?



OR



How does CFT measure up?

I. Colours of Transition Metal Complexes

Why are most transition metal complexes brightly coloured but some aren't?
Why do the colours change as the ligand changes?
Why do the colours change as the oxidation state of the metal changes, even for complexes of the same ligand?

II. Why do different complexes of the same metal ion in the same oxidation state have different numbers of unpaired electrons?

Why are there only certain values of the number of unpaired electrons for a given metal ion?

III. Why do some transition metal ions seem to have a fixed coordination number and geometry, while other metal ions seem variable?

IV. Why do some metal complexes undergo ligand-exchange reactions very rapidly and other similar complexes react very slowly, yet this reaction is thermodynamically favorable?

Course Outline

I. **Introduction to Transition Metal Complexes.**
  - *Classical complexes (Jorgenson and Werner)*
  - *Survey of ligand coordination numbers, geometries and types of ligands*
  - *Nomenclature*
  - *Isomerism*

II. **Bonding in Transition Metal Complexes.**
  - *Electron configuration of transition metals*
  - *Crystal field theory*
  - **Valence bond theory**
  - **Simple Molecular Orbital Theory**
  - *Electronic Spectra and Magnetism*

III. **Kinetics and Mechanisms of Inorganic Reactions.**
  - Stability and lability
  - Substitution reactions
  - Electron transfer reactions

IV. **Descriptive Chemistry of TMs.**

V. **Organometallic Chemistry**
  - 18 e^- rule, σ, and π bonding ligands (synergistic bonding)
  - Metal carbonyls, synthesis, structure, reactions
  - Compounds with delocalized π-conjugated organic ligands.
  - Reactions and catalysis

18- Electron Rule.

Recall that for MAIN GROUP elements the **octet rule** is used to predict the formulae of covalent compounds.

This rule assumes that the central atom in a compound will make bonds such that the total number of electrons around the central atom is **8**. **THIS IS THE MAXIMUM CAPACITY OF THE s and p orbitals.**

This rule is only valid for Period 2 nonmetallic elements.

The **18-electron Rule** is based on a similar concept.

The central TM can accommodate electrons in the s, p, and d orbitals.

s (2) , p (6) , and d (10) = maximum of 18

This means that a TM can add electrons from Lewis Bases (or ligands) in addition to its valence electrons to a total of 18.

This is also known Effective Atomic Number (EAN) Rule

Note that it only applies to metals with low oxidation states.

18 Electron Rule cont'd

Example 1.

$[Co(NH_3)_6]^{+3}$

Oxidation state of Co?
Electron configuration of Co?
Electrons from Ligands?
Electrons from Co?
Total electrons?

Example 2.

$[Fe(CO)_5]$

Oxidation state of Fe?
Electron configuration of Fe?
Electrons from Ligands?
Electrons from Fe?
Total electrons?

What can the EAN rule tell us about **$[Fe(CO)_5]$**?

It can't occur…… 20-electron complex.

EAN Summary

1. Works well only for d-block metals. It does not apply to f-block metals.

2. Works best for compounds with TMs of low ox. state.

3. Ligands which are good σ-donors and π-acceptors utilize all the valence orbitals and thus such compounds obey this rule.

4. Complexes which contain a combination of σ-donors and π-acceptors conform to this rule. (e.g. $Cr(NH_3)_3(CO)_3$, $Cr(\eta^6\text{-}C_6H_6)(CO)_3$).

5. Compounds which obey this rule are kinetically inert to substitution reactions.

6. Exceptions to the rule occur at the two ends of the transition series where *nd, (n+1)s, and (n+1)p* valence orbitals are less well matched in energy.

Let's talk about electron counting briefly.

Sandwich Compounds Obeying EAN

Let’s draw some structures and see some new ligands.

Each of these ligands is π-bonded above and below the metal center.

Ferrocene is an interesting example.

Half-Sandwich Compounds Obeying EAN

Let’s draw some more structures.

CO, NO, H, and PR_3 can be brought together in combination to give 18 electrons.

Some other cool ligands.

These cyclic ligands need not be planar.

Here are some examples of compounds of cyclooctatetraene.

Can a reaction involve only compounds which obey the 18 electron rule?

YES.

Compounds and the EAN Rule

We can divide compounds into three groups.

1. Electronic configurations are completely unrelated to the EAN rule. The central metal may have >, <, = 18 electrons.

2. Electron configurations follow the EAN rule and never have >18 electrons, but may have less.

3. A group that follows EAN rule rigorously.

How can we understand this?

Chemistry and “Magic Numbers”

The Octet Rule: Period 2 nonmetallic elements tend to form compounds resulting in eight electrons around the central atom. You have been told this is because elements desire a pseudo-noble gas configuration.

This is a VAST simplification.

Stable Fullerenes: The allotrope of Carbon known as fullerenes (C_{60} or “Bucky-ball” is the most famous) take on a cage structure and it has been observed that particular numbers of C atoms yield more stable compounds.

C_{60}, C_{70}, C_{76}, C_{84}, C_{90}, C_{94}

Nanoparticles: Metal Nanoparticle are really COOL! It has been observed that “magic numbers” of atoms preferentially come together to form stable structures.

Bonding in TM Complexes: Many TM complexes will form with 18 electrons around the central metal atom. It was first observed by Sedgwick in 1927.

18- Electron Rule.

Recall that for MAIN GROUP elements the **octet rule** is used to predict the formulae of covalent compounds.

Think about Na^+ and Cl^-

This rule assumes that the central atom in a compound will make bonds such that the total number of electrons around the central atom is **8**.

THIS IS THE MAXIMUM CAPACITY OF THE s and p orbitals.

This rule is only valid for Period 2 nonmetallic elements.

The **18-electron Rule** is based on a similar concept.

The central TM can accommodate electrons in the s, p, and d orbitals.

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This means that a TM can add electrons from Lewis Bases (or ligands) in addition to its valence electrons to a total of 18.

This is also known Effective Atomic Number (EAN) Rule

Simple Examples of the 18 Electron Rule

Example 1.

$[Co(NH_3)_6]^{+3}$

Oxidation state of Co?
Electron configuration of Co?
Electrons from Ligands?
Electrons from Co?
Total electrons?

Example 2.

$[Fe(CO)_5]$

Oxidation state of Fe?
Electron configuration of Fe?
Electrons from Ligands?
Electrons from Fe?
Total electrons?

What can the EAN rule tell us about **$[Fe(CO)_5]$**?

It can’t occur…… 20-electron complex.

Approach 1 to counting

Oxidation State Electron Count. Ligands are viewed as "close-shelled" entities. (No radicals). **This is what we did in the earlier examples.**

We dissect the structure

When neutral Lewis base ligands (like NH_3) are considered they are viewed as neutral molecules with 2 electrons for donation to the metal.

Ligands like methyl (CH_3 and Cl) are viewed as anions….**NOT AS NEUTRAL RADICALS.** **(By definition H is viewed as H^-)**

After removal of the ligands the metal is assigned a formal charge.

$[Ni(CO)_4]$	**Ni^0 10 e^-, CO 2 e^- each (8) = 18**
$[PtCl_2(PMe_3)_2]$	**Pt^{2+} 8 e^-, Cl^- 2 e^- each (4), PMe_3 2 e^- each (4) = 16**
$[Ta(Me)_5]$	**Ta^{5+} 0 e^-, Me^- 2 e^- each (10) = 10**
$Fe(\eta^5\text{-}C_5H_5)_2$	**Fe^2 6 e^-, $\eta^5\text{-}C_5H_5$ 6e^- each (12) = 18 Ferrocene**

Approach 2 to counting

Neutral Atom Counting.

The general premise to this approach is:

REMOVE ALL THE LIGANDS FROM THE METAL AS NEUTRAL SPECIES.

This approach results in no difference for neutral ligands like NH_3 or CO.

BUT

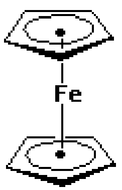
For ligands such as methyl we remove the ligand as a radical. It is therefore a single electron donor in this model.

Furthermore, in this model both the ligand and the metal must donate an electron to the bond.

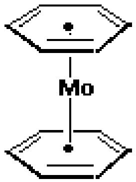
This method provides NO information about the metal oxidation state.

Electron Counting Examples

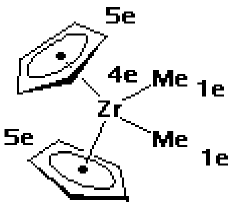
Covalent Counting Rules



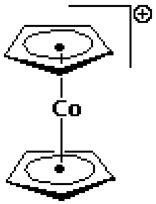
5e
8e
5e
18e



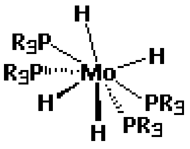
6e
6e
6e
18e



16e

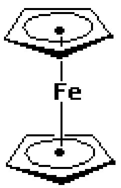


-1e
5e
9e
5e
18e

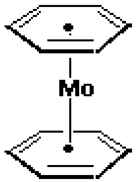


Mo	6e
4 H	4e
4 PR_3	8e
	18

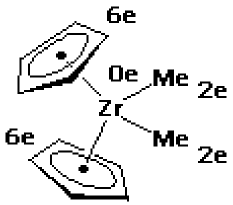
Ionic Counting Rules



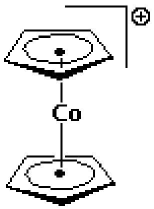
6e ($Cp^{\ominus}$)
6e (Fe^{2+})
6e ($Cp^{\ominus}$)
18e



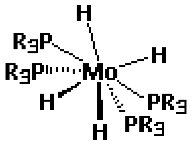
6e
6e
6e
18e



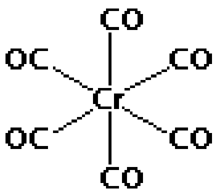
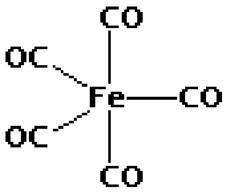
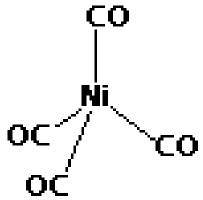
16e



6e ($Cp^{\ominus}$)
6e (Co^{3+})
6e ($Cp^{\ominus}$)
18e

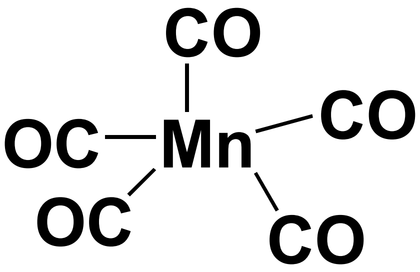


Mo^{4+}	2e
4 H -	8e
4 PR_3	8e
	18

d Group	Formula	Valence electrons		Structure
6	$Cr(CO)_6$	Cr 6 CO	6 12 18	
7	Mn			
8	$Fe(CO)_5$	Fe 5 CO	8 10 18	
9	Co			
10	$Ni(CO)_4$	Ni 4 CO	10 8 18	

Look at CO complexes of Mn

You may expect to have the following structure for a CO complex of Mn.



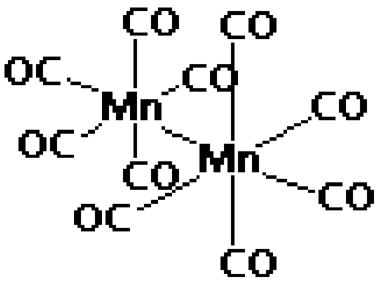
Mn 7
3 CO Terminal 10

Total 17 electrons

7

$Mn_2(CO)_{10}$

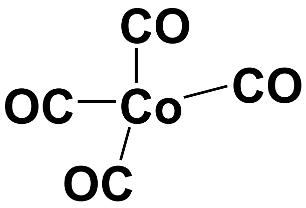
Mn	7
5 CO	10
M-M	1
	18



Prediction of Structure.

(metal carbonyls)

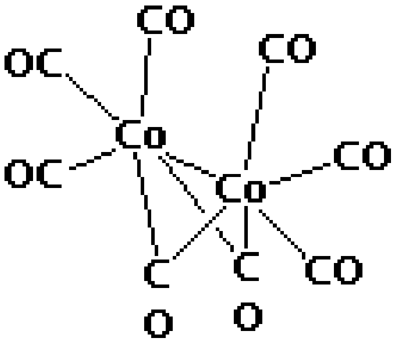
You may expect to have the following structure for a CO complex of Mn.

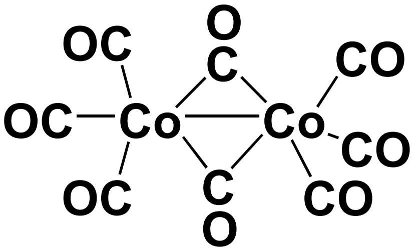


What about ?

$Co_2(CO)_5$

Co 9
3 CO Terminal 6
2 CO Bridging 2
1 Co-Co 1





Is this the only possible structure for bis[tetracarbonylcobalt]?

The EAN Rule cannot differentiate structures of compounds but it CAN provide possibilities for investigation.

Compounds and the EAN Rule

We can divide compounds into three groups.

1. Electronic configurations are completely unrelated to the EAN rule. The central metal may have >, <, = 18 electrons.

2. Electron configurations follow the EAN rule and never have >18 electrons, but may have less.

3. A group that follows EAN rule rigorously.

(This is what I have shown you so far)

How can we understand this?

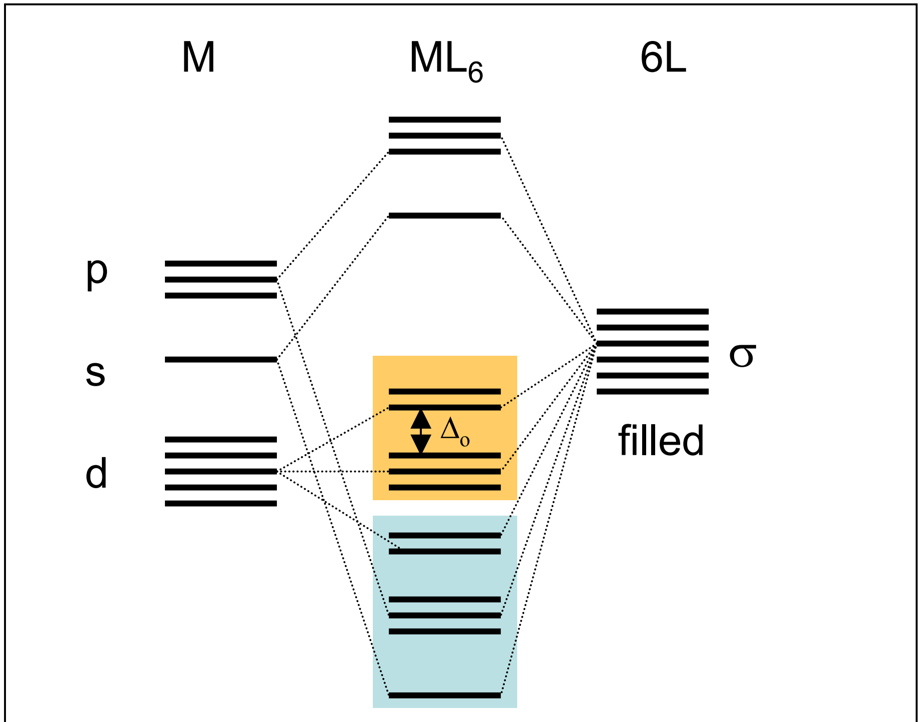
Group I

	(d-electrons, valence)
$\mathrm{TiCl_4(THF)_2}$	(O,12)
$\mathrm{Ti(H_2O)_6^{3-}}$	(1 ,13)
$\mathrm{V(urea)_6^{3-}}$	(2 ,14)
$\mathrm{CrCl_6^{3-}}$	(3 ,15)
$\mathrm{CrI_2(DMSO)_4}$	
$\mathrm{Mn(H_2O)_6^{2+}}$	
$\mathrm{CoF_6^{3-}}$	
$\mathrm{CuCl_5^{3-}}$	
$\mathrm{Ni(H_20)_6^{2+}}$	
$\mathrm{Cu(H_20)_6^{2+}}$	
$\mathrm{ZnCl_2(biuret)_2}$	

You figure out.

Valence electrons from 12 to 22.

Ligands are weak field, Δ_o is small.



Weak sigma interaction and NO pi interaction by 6L

Little or no pi interaction between metals and ligands. Energy of the t_{2g} orbitals is the same as the free metal.

There are 6 low energy bonding MO's, 5 medium energy MO's and and 4 strongly antibonding MO's (too high energy to be occupied).

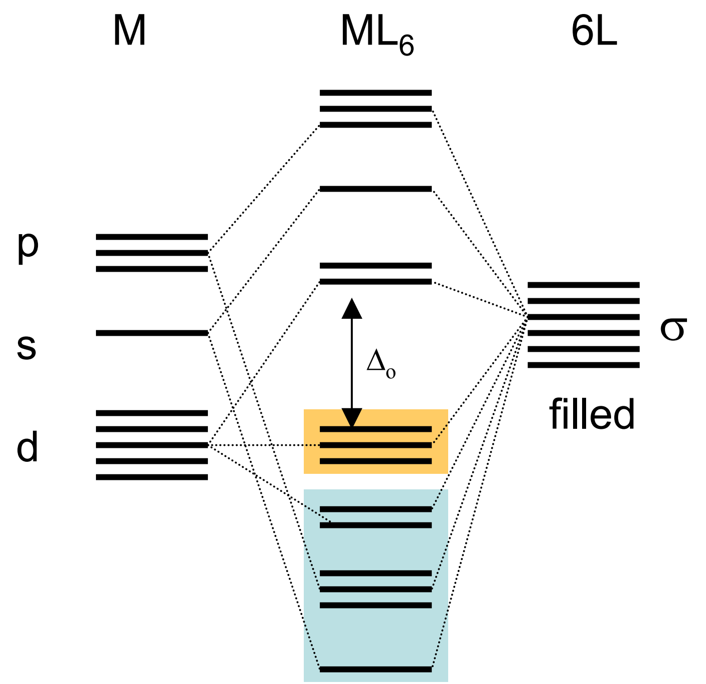
12 electrons from the ligands fill the lowest energy orbitals (blue). Up to 6 metal electrons reside in the t_{2g} set (nonbonding) without any destabilization of bonding.

Δ_o is so small that up to 4 electrons can be put into the e_g set with only a small penalty.

Group II

	(d-electrons, valence)
$Zr(CH_3)_2^{2-}$	(O,12)
$Ti(en)_3^{3--}$	(1 ,13)
$Re(NCS)_6^{-}$	(2 ,14)
$Mo(NCS)_6^{3-}$	(3 ,15)
$Os(SO_3)_6^{8-}$	
$Ir(NH_3)_4Cl_2^{2+}$	
ReH_9^{2-}	

You figure out.



Strong sigma interaction and NO pi interaction by 6L

Valence electrons equal to 12 to 18.

Strong sigma donation increases e_g energy and increases Δ_o .

Little or no pi interaction between metals and ligands. Energy of the t_{2g} orbitals is the same as the free metal. Their occupation has no impact on the stability of the complex.

There are 6 low energy bonding MO’s, 3 medium energy MO’s and and 6 strongly antibonding MO’s (too high energy to be occupied).

12 electrons from the ligands fill the lowest energy orbitals (blue). Up to 6 metal electrons reside in the t_{2g} set (nonbonding) without any destabilization of bonding.

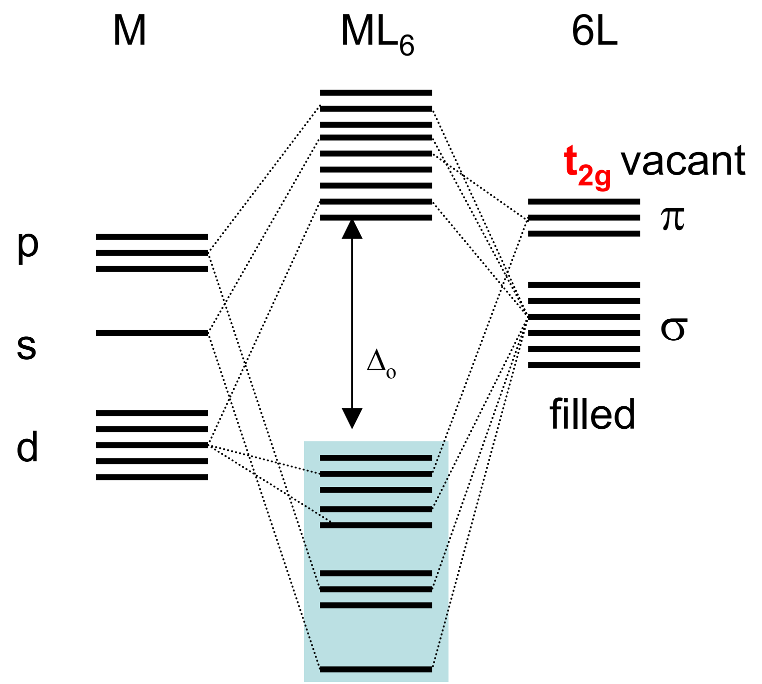
Δ_o is so large that electrons cannot be put into the e_g set without large penalty.

Group III

	(d-electrons, valence)
$Ti(cp)_2(CO)_2$	(4, 18)
$V(CO)_5NO$	(5 ,18)
$Cr(C_6H_6)_2$	(6 ,18)
$MnH(CO)_5$	(7 ,18)
$Fe(NO)_2(CO)_2$	
$Co(NO)(CO)_3$	
$Ni(CO)_4$	

You figure out.

Valence electrons always equal to 18.



Strong sigma interaction and strong pi acceptor interaction by 6L.

Strong sigma donation increases e_g energy
Pi accepting ligands lower t_{2g} energy. BOTH increase Δ_o .

There are 9 low energy bonding MO's,
9 strongly antibonding MO's (too high energy to be occupied).

12 electrons from the ligands and 6 metal electrons in the t_{2g} orbitals fill the lowest energy orbitals (blue). **Removal of the d electrons from the t_{2g} set would destabilize the bonding.**

Δ_o is so large that electrons cannot be put into the e_g set without large penalty.

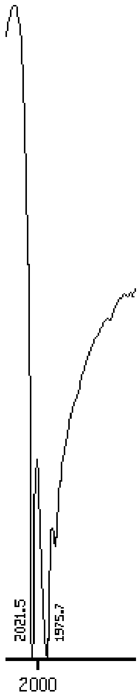
Examples include CO and NO ligands which are at the top of the **SCS**.

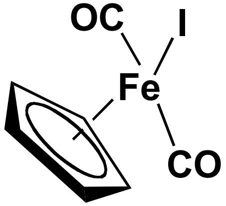
EAN Summary

1. Works well only for d-block metals. It does not apply to f-block metals.
2. Works best for compounds with TMs of low ox. state.
3. Ligands which are good σ-donors and π-acceptors utilize all the valence orbitals and thus such compounds obey this rule.
4. Complexes which contain a combination of σ-donors and π-acceptors conform to this rule. (e.g. $Cr(NH_3)_3(CO)_3$, $Cr(\eta^6\text{-}C_6H_6)(CO)_3$).
5. Compounds which obey this rule are kinetically inert to substitution reactions.
6. Exceptions to the rule occur at the two ends of the transition series where *nd, (n+1)s, and (n+1)p* valence orbitals are less well matched in energy.

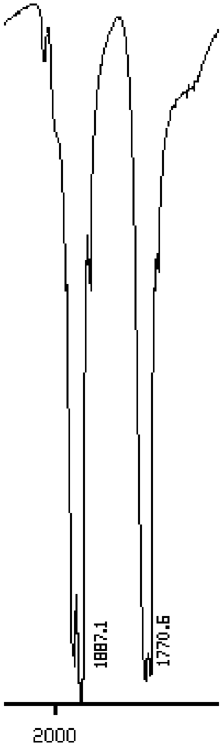
This Rule allows for prediction of structures, reactivity, and reaction mechanisms.

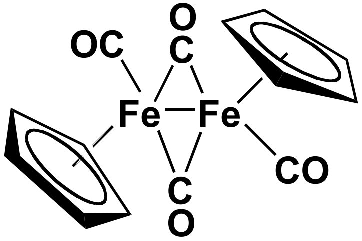
Bridging or Terminal CO





Terminal CO bonding at 2021.5 cm^{-1} and 1975.7 cm^{-1} also, because of very small symmetry differences between carbon monoxides.

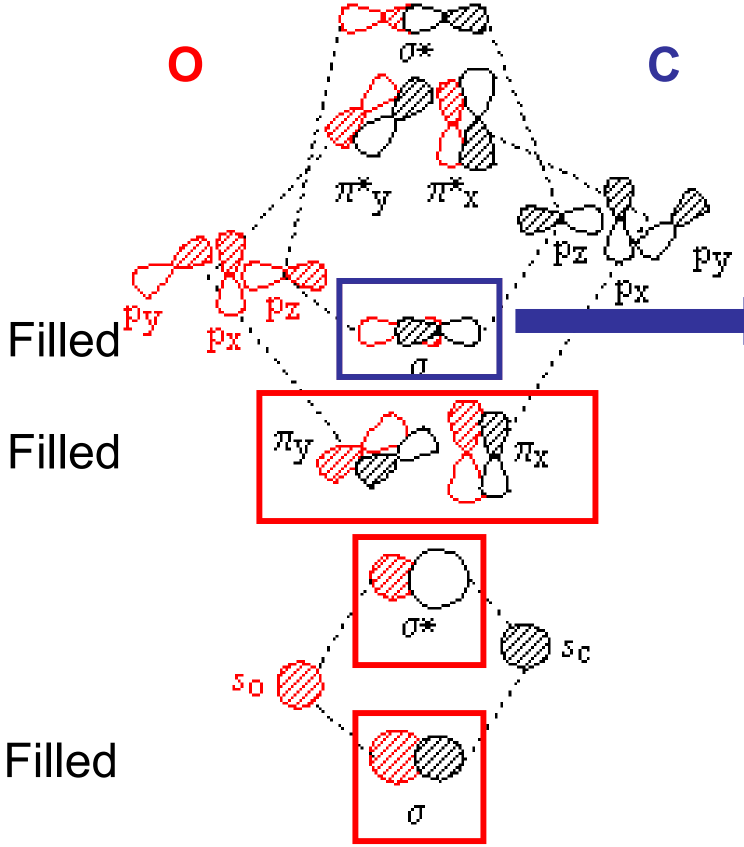




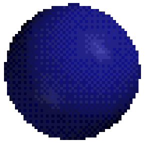
Terminal CO bond1887 cm^{-1}
Bridging CO bond at 1770 cm^{-1}

Bonding in TM Carbonyls

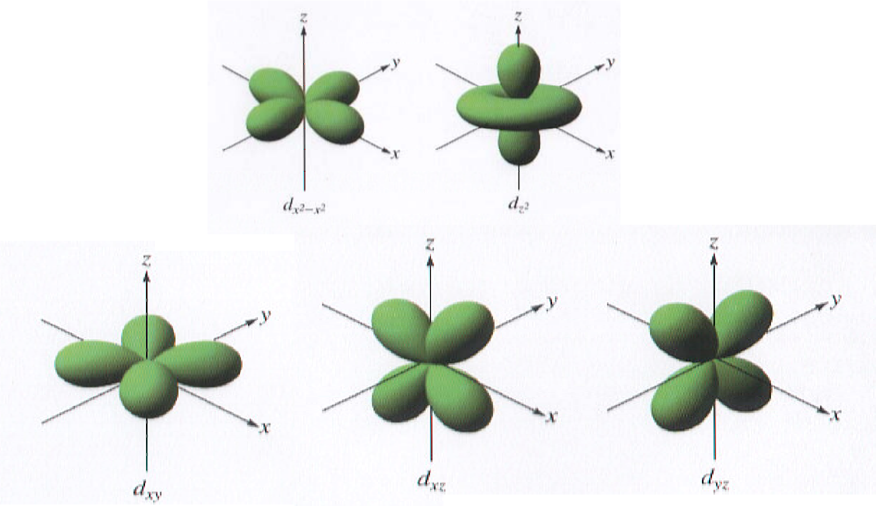
CO bonding-the orbital picture

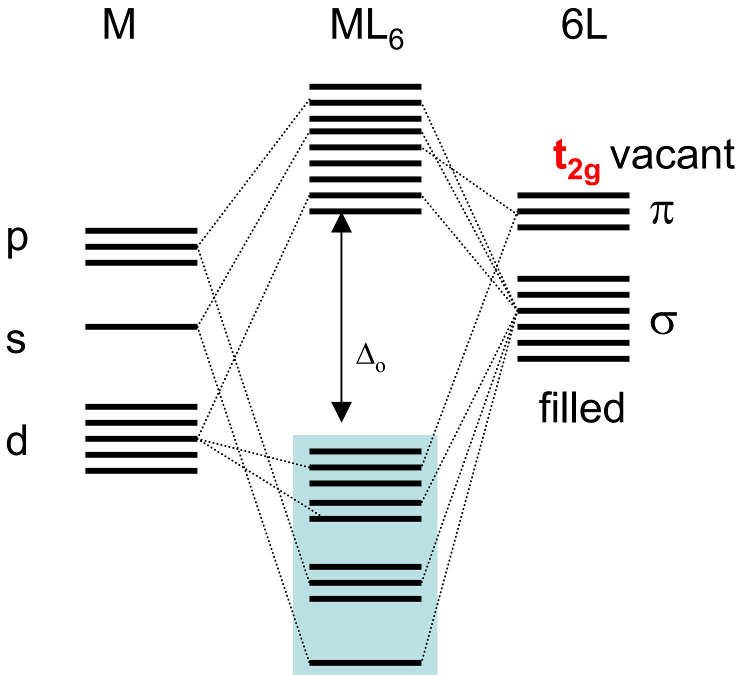


10 valence electrons
C (4), O(6)



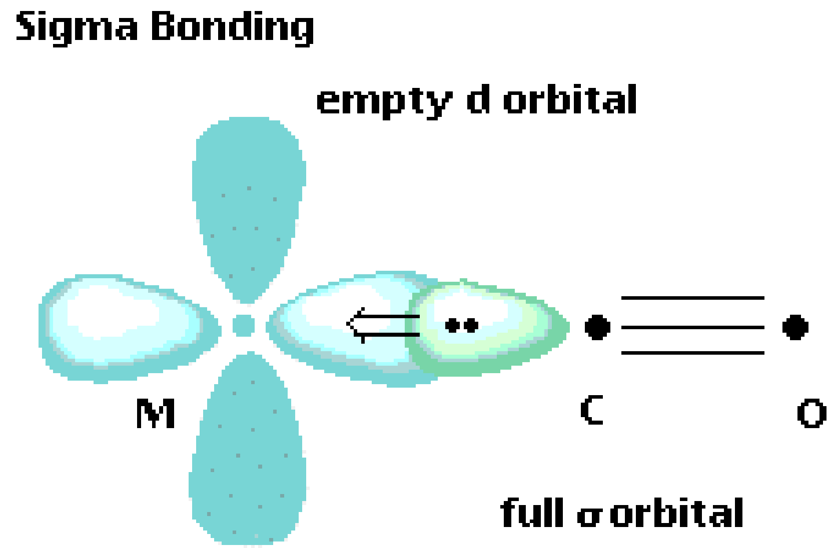
HOMO

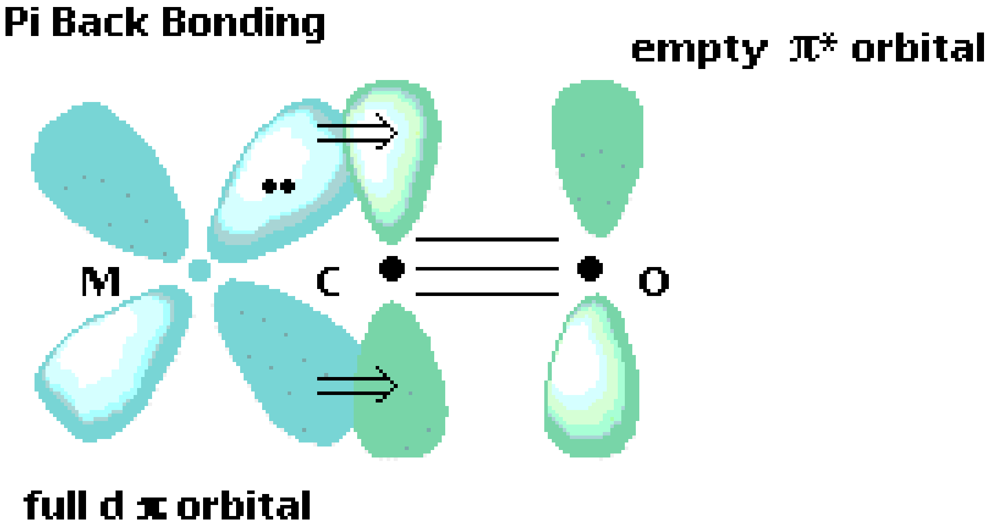




Strong sigma interaction and **strong pi acceptor interaction** by 6L.

A cartoon of M-CO bonding.





The HOMO in carbon monoxide is the high energy σ^{NB} which is primarily derived from a carbon 2p orbital.

This means a lone pair of electrons is residing on the C atom.

The LUMO on CO is the π^*_{2p} which are antibonding orbitals with significant 2p character.

CO acts as a Lewis Base and a Lewis Acid.

The back bond appearing in this systems is known as a **synergistic effect**.

Reactions of Metal Carbonyls.

i) Substitution of CO by other L

(L is often a π-acid or Soft Lewis base; L= PR_3, polyolefins, SR_2, CH_3CN)

Recall that TM carbonyls obey the 18 electron rule.

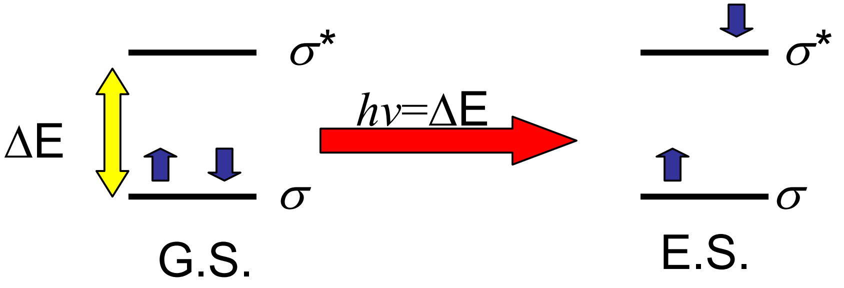
This means two things….

They are inert toward substitution.

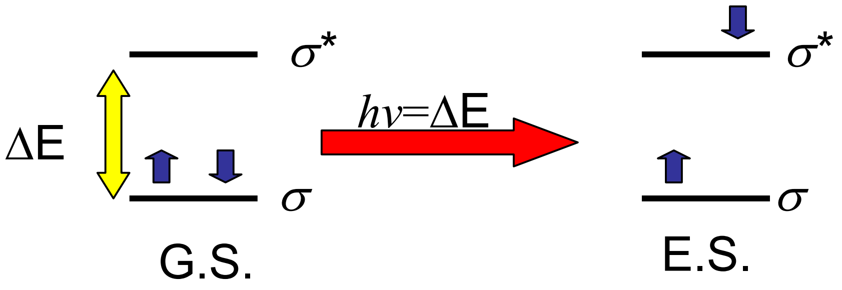
Reactions must proceed via a Dissociative mechanism (via M-CO bond cleavage)

This provides a basis for photochemistry:

If light of a suitable energy is supplied such that $\sigma \Rightarrow \sigma^*$ can occur some interesting things happen.



M-CO Photochemistry



B.O.= 0

This negates the M-CO σ bond.

Bond Order = 1/2 (electrons in bonding orbitals - electrons in anti-bonding orbitals)

CO is photoejected!

$$L_nM\text{-}CO \xrightarrow[\textit{slow}]{h\nu} [L_nM] \xrightarrow[\textit{fast}]{L'} L_nM L'$$

18 electrons

slow
- CO

16 electrons
High energy
reactive intermediate.

fast

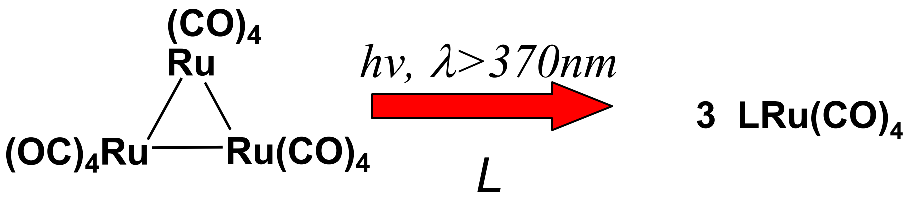
18 electrons

ΔE~390nm

In theory, by filtering the excitation light it should be possible to remove only 1 CO.

This is not simple given the broad nature of the UV-vis bands.

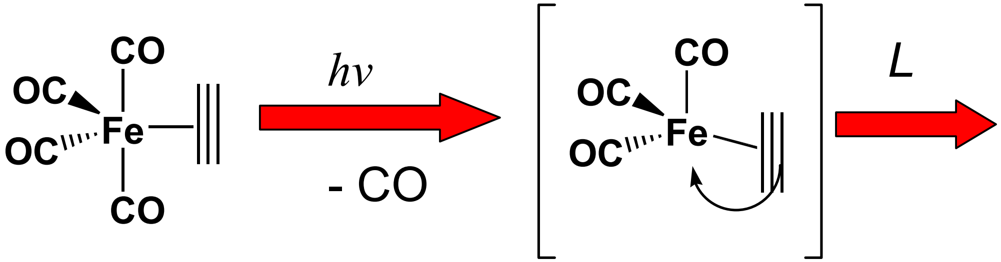
M-CO photochemistry Examples



(L= olefin)

Orange, colour arises from $\sigma \Rightarrow \sigma^*_{(Ru\text{-}Ru)}$ λ~390nm

Another example involving Fe and an 18 electron transition state



18 electrons
alkyne 2e$^-$ donor

18 electrons
alkyne 4e$^-$ donor

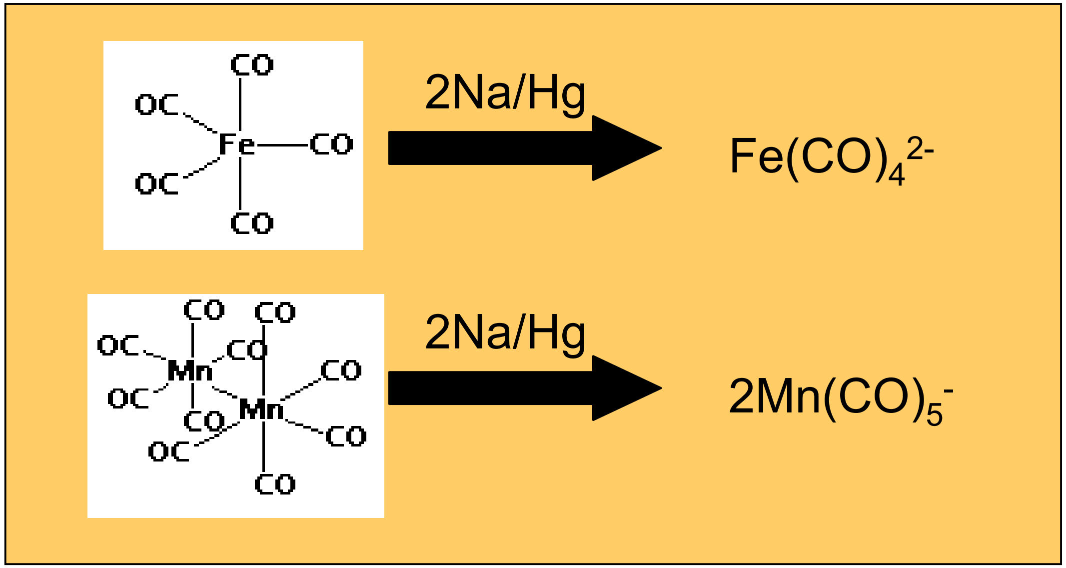
This intermediate is not 16e- and is stabilized by a 4e- donor alkyne.

It substitutes 10^{13}x faster than $Fe(CO)_5$.

Reduction of TM Carbonyls

What will happen if electrons are added to 18e$^-$ TM carbonyls?

High energy 19 or 20 electron systems will result and CO will be ejected. (This can be viewed as the two electrons taking the place of the CO or breaking M-M bonds)

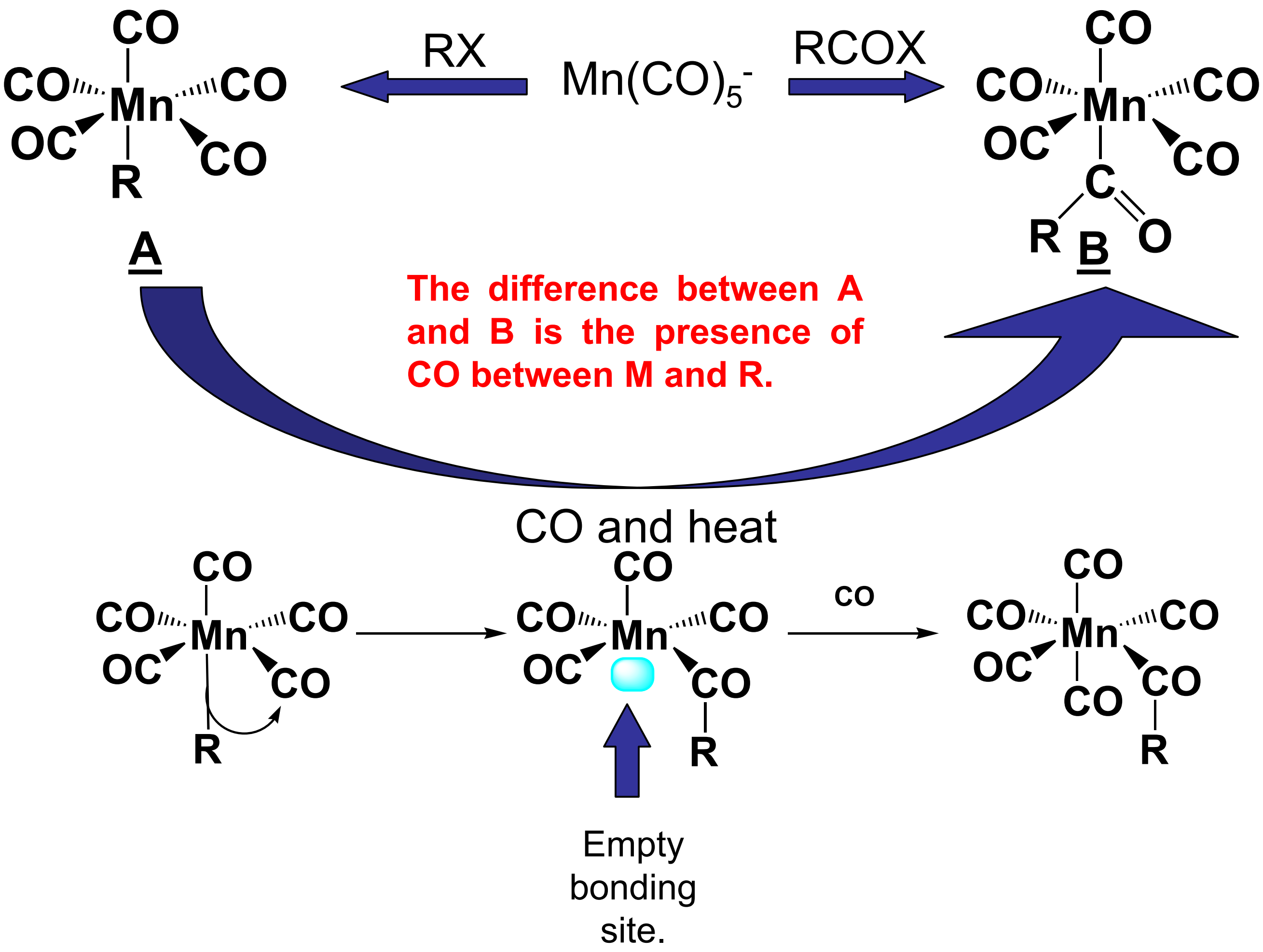


2Na/Hg → $Fe(CO)_4^{2-}$

2Na/Hg → $2Mn(CO)_5^-$

These anions are of significant importance. They are nucleophiles and react further to form M-C and M-H bonds.

Formation of M-H and M-C bonds



The difference between A and B is the presence of CO between M and R.

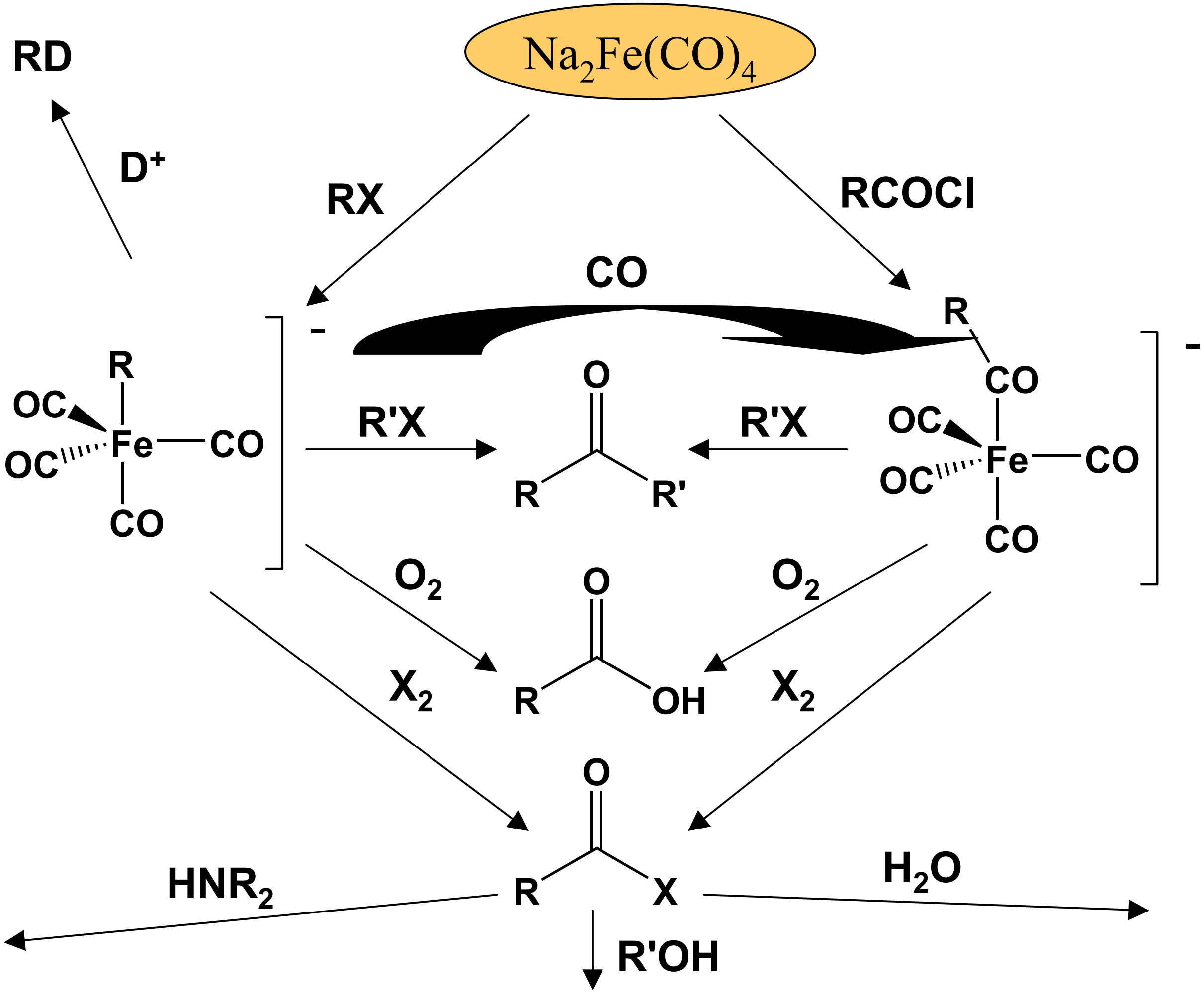
Empty bonding site.

This is referred to as “CO insertion” although the mechanism involves migration of R.

$$Mn(CO)_5^- + H^+ \longrightarrow H\text{-}Mn(CO)_5^-$$

Collman’s Reagent

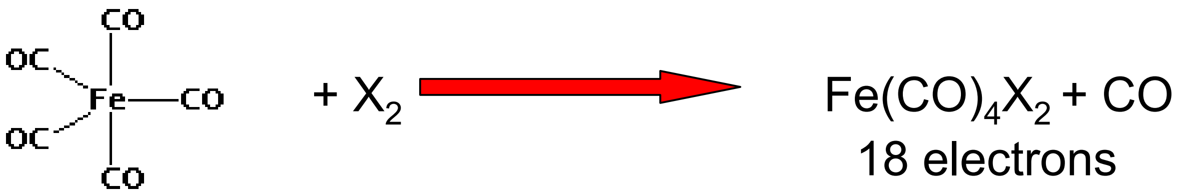
Application of “carbonylmetallates” in organic synthesis.



Disodium tetracarbonylferrate is useful in the functionalization of organic halides.

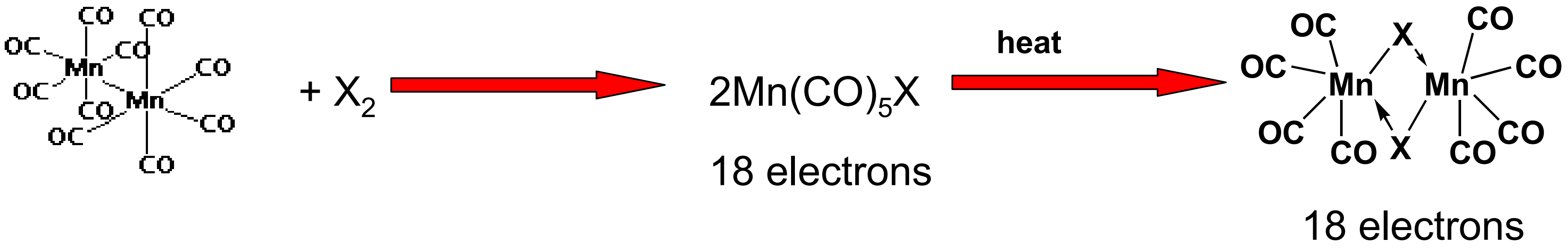
Oxidation of TM Carbonyls

Oxidation weakens the M-CO or M-M bonds and results in CO elimination or M-M cleavage with the formation of TM carbonyl halides.



$+ X_2 \rightarrow Fe(CO)_4X_2 + CO$

18 electrons



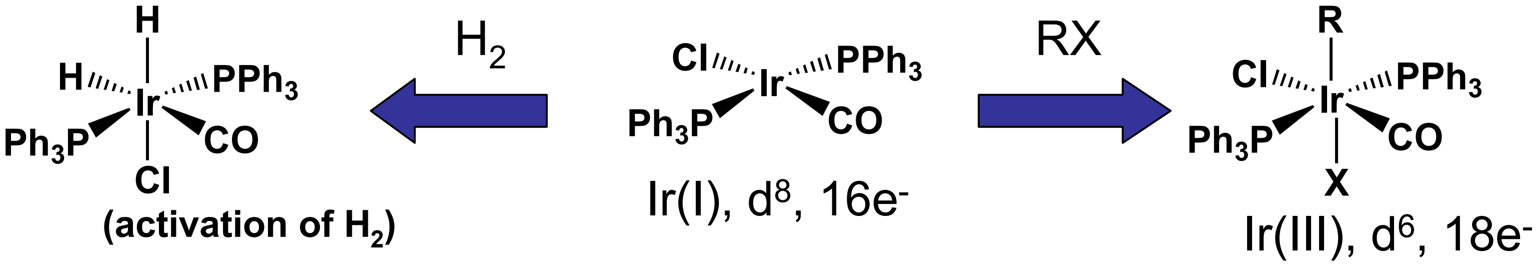
$+ X_2 \rightarrow 2Mn(CO)_5X$

18 electrons

18 electrons

$$Mn(CO)_5X \xrightarrow[RMgX]{RLi} Mn(CO)_5R$$

Special Case. Oxidative Addition (4-coordinate Vaska's Compound 1961, 16 electron species)



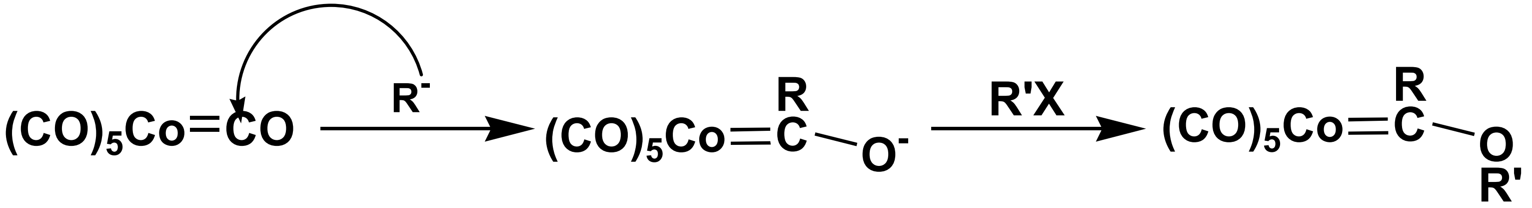
(activation of H_2)

Ir(I), d^8, $16e^-$

Ir(III), d^6, $18e^-$

Reactions of Coordinated M-CO

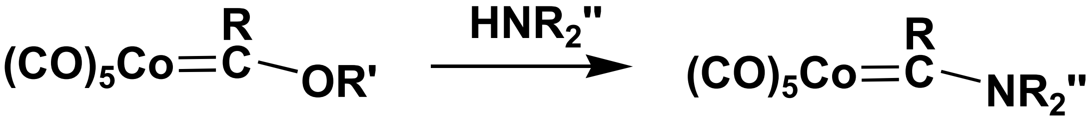
The attachment of CO to a TM makes the C electrophillic and may be attacked by a nucleophile)



$$(CO)_5Co{=}CO \xrightarrow{R^-} (CO)_5Co{=}\overset{R}{C}-O^- \xrightarrow{R'X} (CO)_5Co{=}\overset{R}{C}-OR'$$

This is a carbene complex; E.O. Fischer discovered this type of molecule and shared the Nobel Prize with Wilkinson.

The “$(CO)_5Co$” structural unit acts as an electron withdrawing; It is a pseudo ester.

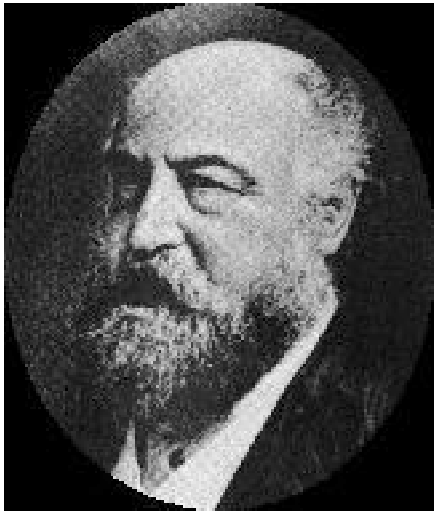


$$(CO)_5Co{=}\overset{R}{C}-OR' \xrightarrow{HNR_2''} (CO)_5Co{=}\overset{R}{C}-NR_2''$$

Trans-esterification

The Mond Process

Nickel carbonyl, a gas formed from carbon monoxide and metallic nickel.

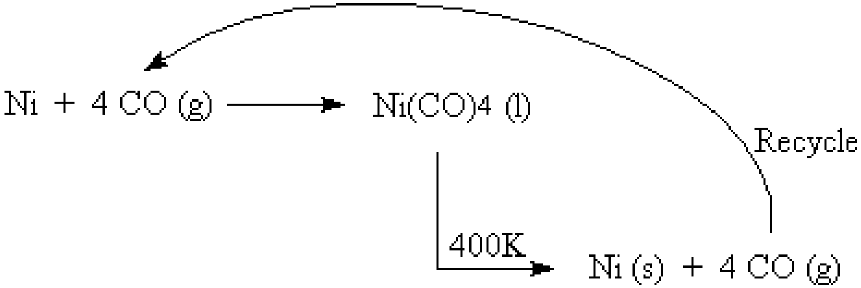


Scientific Serendipity

In 1890 Ludwig Mond, was investigating the rapid corrosion of nickel valves used in apparatus for the **Solvay process***, and discovered $Ni(CO)_4$.

In contrast to many nickel compounds which are usually green solids, $Ni(CO)_4$ is a colourless, volatile, toxic liquid with a very "organic character".

He used it as the basis of a method to purify nickel, called the **"Mond process".**

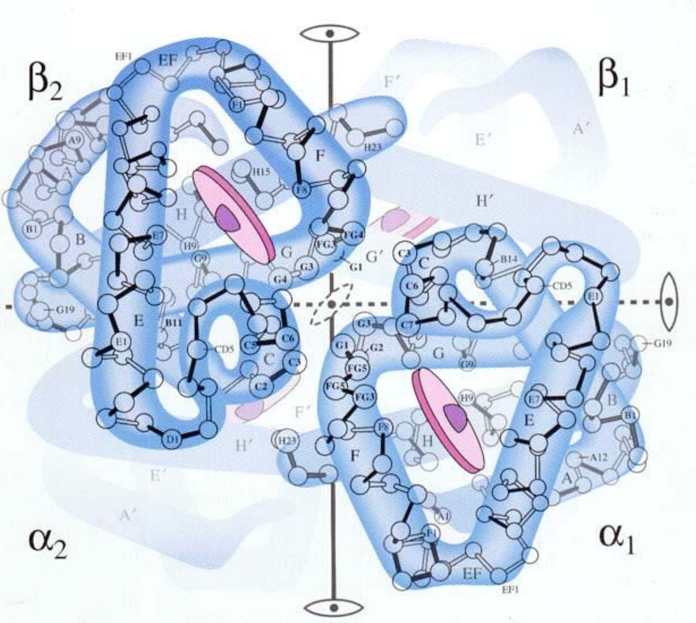


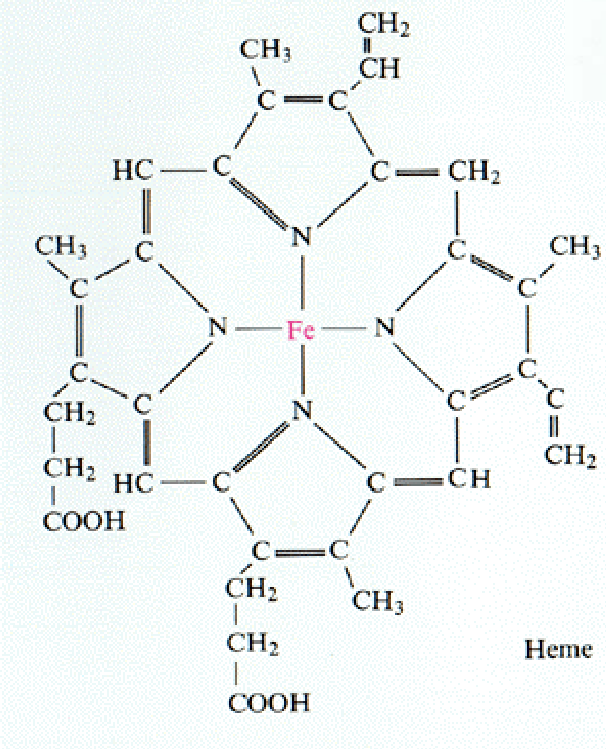
Ni reacts with CO (leaving the impurities behind), to form $Ni(CO)_4$.

The $Ni(CO)_4$ is passed through a tower filled with nickel pellets at a high velocity and 400 K.
Pure Ni plates out on the pellets.

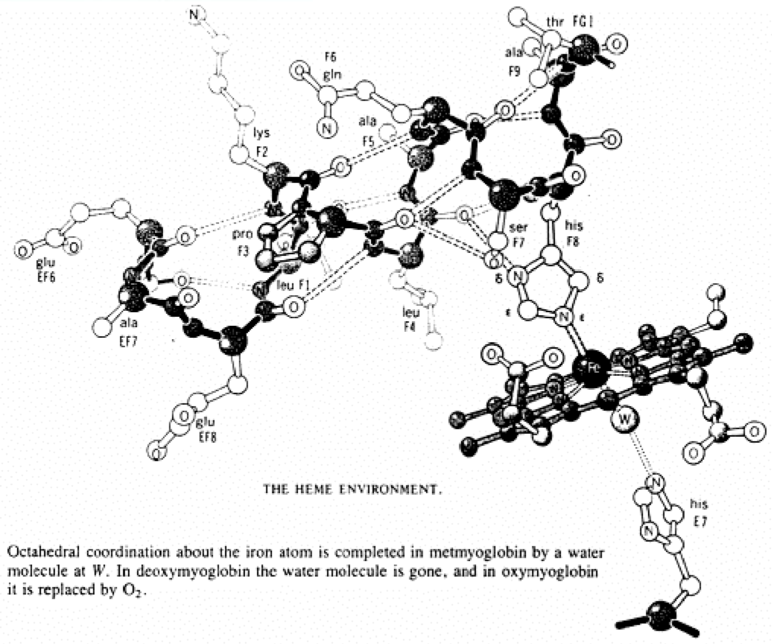
* A commercial process for the manufacture of Na_2CO_3. NH_3 and CO_2 are passed into a sat'd $NaCl_{(aq)}$ solution to form soluble $(NH_4)(HCO_3)$, which reacts with the NaCl to form soluble NH_4Cl and solid $NaHCO_3$ if the reactor temperature is maintained below 15°C. The $NaHCO_3$ is filtered off and heated to produce Na_2CO_3.

Hemoglobin and Heme





Heme



THE HEME ENVIRONMENT.

Octahedral coordination about the iron atom is completed in metmyoglobin by a water molecule at *W*. In deoxymyoglobin the water molecule is gone, and in oxymyoglobin it is replaced by O_2.

Formation and Reactions of TM Complexes

What have we done so far?

1. What is the structure of these compounds?
   (Coordination Number, Geometry, Isomerization)

2. What holds these complexes together and how do we study them?
   (CFT d-orbital splitting, electronic spectroscopy, MO theory)

But….you can't study them if you can't get them…..

How are they made?

Where do we start?

How about with a Co and Pt complex? **$[Co(en)_2(NO_2)_2]^+$**, and **cis/trans platin.**

This is an interesting case:

We start with a Co^{2+} salt….**what is the oxidation state of Co in the product?**

Why do we use the Co^{2+}?

Ligand substitution occurs more readily than with Co^{3+}… but why?

$$CoCl_{2(aq)} \quad \boxed{\{[Co(OH_2)_6]Cl_2\}} \xrightarrow[2NO_2^-]{2\text{ en}} \xrightarrow{O_2} [Co(en)_2(NO_2)_2]^+$$

If we change our starting material we can control stereochemistry…. but why?

$$[PtCl_4]^{2-} + 2NH_3 \longrightarrow \textit{cis}\text{-}PtCl_2(NH_3)_2$$

$$[Pt(NH_3)_4]^{2+} + 2Cl^- \longrightarrow \textit{trans}\text{-}PtCl_2(NH_3)_2$$

Why do these reactions occur the way they do?
We are going to look at influencing factors and mechanisms.

Stable vs. Unstable
Inert vs. Labile

When TM ions are dissolved in water the ions form aqua complexes.

UV-Vis, NMR indicate a six-coordinate octahedral species for 1st row TMs.

$$[M(OH_2)_6]^{2+/3+}$$

(neutron diffraction of these species was first reported in 1984)

Given that the ions are not "free" in solution, formation of TM complexes involves the replacement (substitution) of one ligand with another.

$$[M(OH_2)_6]^{2+/3+} + nL \longleftrightarrow [ML_n]^{x+}$$

That these reactions occur in aqueous solution is VERY important to numerous disciplines including Inorganic Chemistry, Biochemistry, Analytical Chemistry, Environmental Chemistry and other applications.

TM Aqua Complexes

An IMPORTANT point about TM-aqua complexes.

The amount of time (residence time) the H_2O ligands spends attached to the TM can vary significantly from metal to metal.

$[Cr(OH_2)_6]^{3+}$ and $[Co(OH_2)_6]^{3+}$ fail to exchange with $^{18}OH_2/^{17}OH_2$ after several hours.

$$[Cr/Co^{16}(OH_2)_6]^{3+} + \text{large XS } ^{18}OH_2/^{17}OH_2 \xleftrightarrow{\text{hours}} [Cr/Co^{18/17}(OH_2)_6]^{3+}$$

Most other TMs exchange water rapidly.

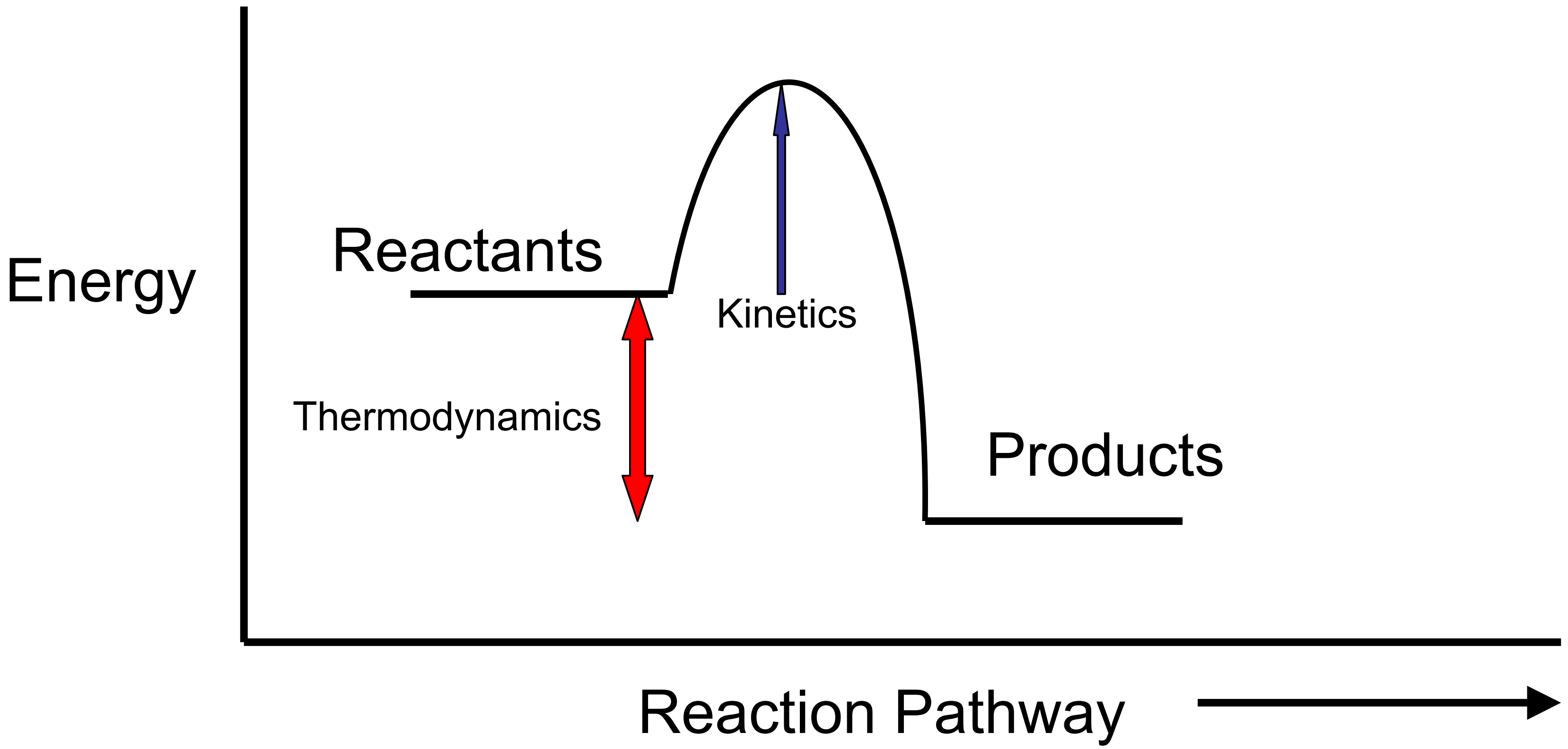
What does this tell us about formation of TM complexes and what we need to consider?

1. **Thermodynamics**: When examining thermodynamics of a reaction we are entirely interested in the start and finish of a reaction. What is the extent of reaction? Where does the equilibrium lie? **How do we investigate this?**

ΔG^o

2. **Kinetics:** How fast does a reaction reach equilibrium? This relates directly to the mechanism.

Look at the reaction coordinate diagram…



Kinetics vs. Thermodynamics

We use terms to describe the Thermodynamic and Kinetic aspects of reactivity.

Thermodynamic. Stable or Unstable

Kinetic. Inert or Labile

An inert compound is not "inert" in the usual sense that no reaction will occur. Rather, the reaction takes place slower than for labile compounds.

There is NO connection between Thermodynamic Stability/Instability of a complex and its Lability/Inertness toward substitution.

For example:

Stable …but labile

$[Ni(CN)_4]^{2-} + 4\,{}^{13}CN^- \longleftrightarrow [Ni({}^{13}CN)_4]^{2-} + 4CN^-$ $t_{1/2} \sim$ 30sec.

$[Ni(CN)_4]^{2-} \longleftrightarrow Ni^{2+}_{(aq)} + 4CN^-_{(aq)}$ $K_{eq} = 1 \times 10^{-30}$

Unstable but inert

$[Co(NH_3)_6]^{3+} + 6H_2O \longleftrightarrow [Co(OH_2)_6]^{3+} + 6NH_4^+$ $t_{1/2} \sim$ days.

$K_{eq} = 1 \times 10^{25}$

Conclusions from these examples.

Stable complexes have a large POSITIVE ΔG^o_{RXN} for ligand substitution and Inert complexes have a large POSITIVE $\Delta G^\ddagger$ (activation).

Stability and Coordination Complexes ($[ML_n]^{x+}$)

Typically expressed in terms of an overall formation or stability constant. (This is K_{st} on the Chemistry Data sheet you receive with exams)

$$[M]^{x+} + nL \longleftrightarrow [ML_n]^{x+} \qquad K_{st} = \frac{[ML_n]^{x+}}{[M^{x+}_{(aq)}][L]^n}$$

BUT, this does not occur in one fell swoop!!
Water molecules do not just all fly off and are immediately replaced by nL ligands.

$$[M]^{x+}_{(aq)} + L \longleftrightarrow [ML]^{x+} \qquad K_1$$

$$[ML_{(n-1)}]^{x+} + L \longleftrightarrow [ML_n]^{x+} \qquad K_n$$

K_s are the stepwise formation constants and provide insight into the solution species present as a function of [L].

Stepwise formation constants

These formation constants provide valuable information given that different species may have VERY DIFFERENT properties…including environmental impact. Such information provides selective isolation of metal ions from solution through reaction with ligands.

For formation of divalent alkaline earth and 3d M^{2+} TM ions the **Irving-Williams Series** holds true.

Ba<Sr<Ca<Mg<Mn<Fe<Co<Ni<Cu>Zn

What is contributing to this trend?

1. Charge to radius ratio.
2. CFSE (beyond Mn^{2+})
   Jahn-Teller Distortion
3. Hard-Soft Acids/Bases

See R-C p 450-451.

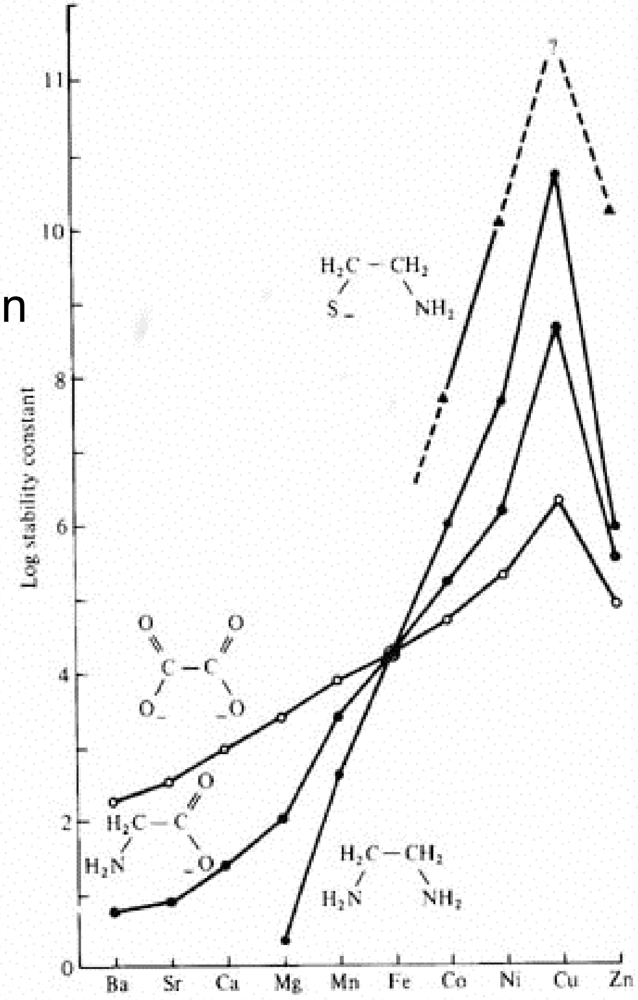


Fig. 9.5 The Irving–Williams effect: The stability increases in the series Ba–Cu, decreases with Zn. [From Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201. Reproduced with permission.]

The Pearson LA/LB "Hard"/"Soft" Approach

Hard Lewis Bases: high EN, low polarizability, hard to oxidize: O, N, F^- donors (Cl^- is borderline).

Soft Lewis Bases: low EN, highly polarizable, easy to oxidize: S, P, I^-, Br^-, R^-, H^- donors.

Hard Lewis Acids: small, highly charged (high ox. State): H^+, alkali metal (M^+) and alkaline earth (M^{2+}) cations, Al^{3+}, Cr^{3+}, BF_3.

Soft Lewis Acids: large, low oxidation state: Cu^+, Ag^+, Au^+, Tl^+, Hg^{2+}, Pd^{2+}, Pt^{2+}, BH_3

In this model, hard acids "like" hard bases and soft acids "like" soft bases.

Chelate Effect

$[Ni]^{2+} + 6\ NH_3 \longleftrightarrow [Ni\ (NH_3)_6]^{2+}$ log K_{st} = 8.61

$[Ni]^{2+} + 3\ en \longleftrightarrow [Ni\ (en)_3]^{2+}$ log K_{st} = 18.28

Both ligands have a N-donor, yet the en complex is 10 orders of magnitude more stable than the $NH_{3.}$

This is a general effect that a complex with one (or more) 5 or 5-membered rings has a greatly enhanced stability relative to the similar complex lacking rings.

Why is this happening? What's missing from our equation?

$[Ni(OH_2)_6]^{2+} + 6\ NH_3 \longleftrightarrow [Ni\ (NH_3)_6]^{2+} + 6H_2O$ log K_{st} = 8.61

$[Ni\ (OH_2)_6]^{2+} + 3\ en \longleftrightarrow [Ni\ (en)_3]^{2+} + 6H_2O$ log K_{st} = 18.28

In the GAS PHASE there is no difference in K_{st}

Reactions of Coordination Complexes

The reactions of Coordination Complexes may be divided into three classes:

i) Substitution at the metal center
ii) Reactions of the coordinated ligands
iii) Oxidation and Reduction reactions at the metal center.

For the purposes of our discussion we will confine our discussion to (i) for substitution reactions on **Octahedral** and **Square Planar** complexes.

We will only briefly discuss one specific reaction involving a coordinated ligand.

Rxns of Octahedral Complexes

Consider ML_5X : In this complex there are 5 inert ligands (L) and one labile ligand (X).

For our purposes we will consider the replacement of X with an incoming ligand Y.

$$ML_5X + Y \longrightarrow ML_5Y + X$$

How might this happen?

We need to look at the molecular components.

What elemental steps will result in this process….

In more technical terms: What is the mechanism of this reaction?

There are Two Extreme Cases

Dissociative Mechanism (D) Associative Mechanism (A)

Dissociative Mechanism

$$ML_5X + Y \longrightarrow ML_5Y + X$$

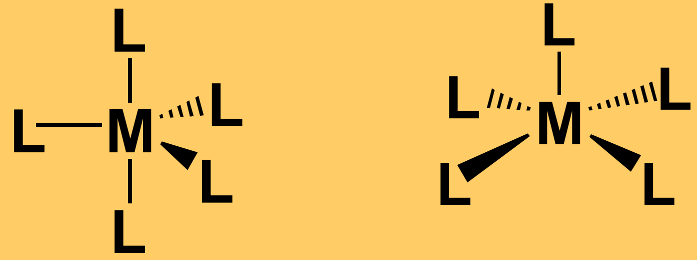
Step 1. Dissociation of X to yield a 5 coordinate intermediate.

$$ML_5X \xrightarrow{K_1} ML_5 + X$$

M-X bond is broken

Slow and *rate determining*

The rate of D is only depends on the conc. of ML_5X



Trigonal Bipyramidal **Square Pyramidal**

Step 2. Coordination of Y to the ML_5 intermediate.

$$ML_5 + Y \xrightarrow[\text{fast}]{K_2} ML_5Y$$

This mechanism is independent of [Y]

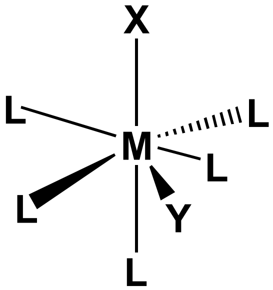
The rate law for this process is rate = $K_1[ML_5X]$ (the units of K_1 are sec^{-1})
If we find a reaction follows this rate law we conclude it is dissociative.

Associative Mechanism

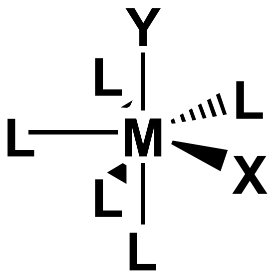
$$ML_5X + Y \longrightarrow ML_5Y + X$$

Step 1. Collision of ML_5X with Y to yield a 7-coordinate intermediate. (slow)

$$ML_5X + Y \xrightarrow{K_1} ML_5XY \qquad \text{(slow, rate determining)}$$



Capped Octahedron



Pentagonal Bipyramid

Step 2. Cleavage of the M-X bond. (fast)

$$ML_5XY \longrightarrow ML_5Y + X \qquad \text{(fast)}$$

The rate law for this process is rate = $K_1[ML_5X][Y]$ (the units of K_1 are $sec^{-1}Mole^{-1}$)
If we find a reaction follows this rate law we conclude it is associative.

Telling the difference…

By determining the rate law (uni- vs. bi- molecular) we can determine the mechanism of the reaction in question.

rate = $K_1[ML_5X]$ **or** **rate = $K_1[ML_5X][Y]$**

This is achieved via monitoring the disappearance reactant(s) and the appearance of product(s) using spectroscopic methods and variations in reactant concentrations.

This is not always as simple as we see here….

We will discuss one complication.

Solvents and Water!!

Often experimental conditions “mask” the dependence upon [Y].

When a reaction is carried out in a solvent….the solvent is in HUGE excess and it is not necessarily “innocent” (it can take a role in the rxn)

What is the concentration of water?

Effectively constant at 55.5M.
Be sure you can determine this!!

Given the excess of water, its concentration remains seemingly constant. As a result, the influence of the water on the mechanism is “masked”. This results in a pseudo-first order rate law.

Solvent and Associative Processes

$$ML_5X + Y \xrightarrow{H_2O} ML_5Y + X$$

Step 1. Collision of ML_5X with Y or H_2O to yield a 7-coordinate intermediate.

Given the $[H_2O]$ >>>>[Y] it is much more likely that a collision with H_2O will occur.

$$[ML_5X] + H_2O \xrightarrow{K_1} [ML_5X(O\,H_2)] \qquad \text{(slow, rate determining)}$$

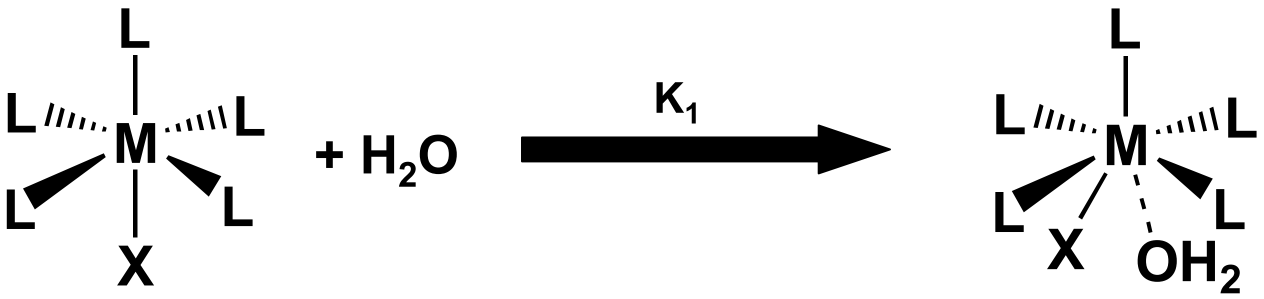
Step 2. Cleavage of the M-X bond.

$$[ML_5X(OH_2)] \xrightarrow{K_2} [ML_5OH_2] + X \qquad \text{(fast)}$$

Step 3 Formation of the M-Y bond.

$$[ML_5X(OH_2)] + Y \xrightarrow{K_3} [ML_5OH_2] + X \qquad \text{(fast)}$$

Looking at the structures…



Rate Law

$$
\begin{aligned}
\text{Rate} = \quad [\text{overall rate}] &= k_1[ML_5X][H_2O] \\
&= \{k_1[H_2O]\}\,[ML_5X] \\
&= K\,[ML_5X]
\end{aligned}
$$

Given the $[H_2O]$ is constant the rate appears to follow a pseudo-1st order rate law.

To determine if the process follows A or D mechanism we need to do other exps.

ML_6 Preferred Mechanism

Octahedral complexes tend to favor a *D* mechanism through a 5 -coordinate intermediate.

$$\mathbf{[M(OH_2)_6]^{X+} + {}^{17}OH_2 \longleftrightarrow [M(OH_2)_5\,{}^{17}(OH_2)]^{X+}}$$

We already discussed that the residence time of H_2O varies a lot.
$1x10^{10}$ s^{-1} to $1x10^{-8}s^{-1}$

M^{X+}	K_1 (s^{-1})
Cs^+	$5x10^9$
Li^+	$5x10^8$
Ba^{2+}	$2x10^9$
Be^{2+}	$2x10^2$

As the charge/radius ratio increases the rate of water exchange decreases.

What obs. of M^{2+} and M^+ can be made?

Charge/Radius Ratio

Given the M-OH_2 bond strength increases as the charge/radius ratio increases, data are consistent with a mechanism where the intermediate was obtained from the cleavage of the M-OH_2 bond and a new M-*OH_2 bond is formed quickly.

This is Characteristic of a Dissociative Mechanism

Exceptions to the charge/ratio rule exist:

Ni^{2+}(0.83Å), Cr^{2+}(0.94Å), Cu^{2+}(0.87Å) very similar size

Ni^{2+}(K_1= $1x10^4 s^{-1}$), Cr^{2+}/Cu^{2+}(K_1= $1x10^9 s^{-1}$) very different rates.

Some inert TM ions that exchange H_2O very slowly:

Cr^{3+}, LS Co^{3+} and sqr. planar Pt^{2+}

The inert nature of these complexes made it possible for Werner to work out his theory.

Inert/Labile d-electron configurations

Generally, INERT *oct.* complexes have large CFSE*, specifically

d^3, and L.S. d^4-d^6

Other compounds tend to be labile.

(dividing line labile vs. inert is t1/2 of 1 min. at 25°C)

	Inert Complexes	Labile Complexes
Octahedral	d3 and LS d^4,d^5,d^6	d^1,d^2,d^7, d^8,d^9,d^{10} HS d^4,d^5,d^6
Sqr. Planar	d^8 Pt^{2+}	Ni^{2+}

Pd^{2+}
(intermediate)

This summary applies best for 3d TMs.

If you consider 4d and 5d metals it is found that these metals have greater CFSE and achieve sigma bonds with better overlap than 3d metals.Hence, such systems tend to be inert on the above time scale.

Why look at water exchange?

The study of simple water exchange reactions is important and valuable given the rate at which $M(OH_2)_6^{X+}$ aqua ions combine with other ligands (L) to form other complexes…..

Shows little or no dependence on L

Rates for each metal ion are practically the same as the rate of exchange for H_2O on the same metal ion.

We can use exchange reactions to provide insight into other substitution reactions.

Anation Reactions

$$[M(OH_2)_6]^{X+} + X^- \longrightarrow [M(OH_2)_5X]^{(X-1)+} + H_2O$$

This type of reaction is important as its behavior indicates not only how new complexes are formed but also where coordinated water is replaced by X^-.

$$[L_5M(OH_2)]^{X+} + X^- \longrightarrow [L_5MX]^{(X-1)+} + H_2O$$

Generally two observations can be drawn:

1. For a given aqua ion, the rate of anation show little dependence on the nature of L.
2. The rate constant for anation of a given aqua complex is almost the same as for H_2O exchange.

These are consistent with a dissociative mechanism…..WHY?

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Anation Reactions

$$[M(OH_2)_6]^{X+} + X^- \xrightarrow{K_a} [M(OH_2)_5X]^{(X-1)+} + H_2O$$

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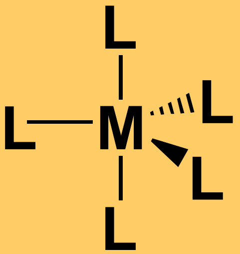
Which Mechanism

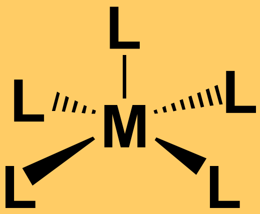
$$ML_5X + Y^- \longrightarrow [ML_5Y]^- + X$$

Step 1. Dissociation of X to yield a 5 coordinate intermediate.

$$ML_5X \xrightarrow{K_1} ML_5 + X$$



Trigonal Bipyramidal



Square Pyramidal

M-X bond is broken

Slow and *rate determining*

The rate of D is only depends on the conc. of ML_5X

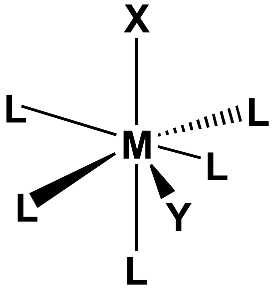
OR

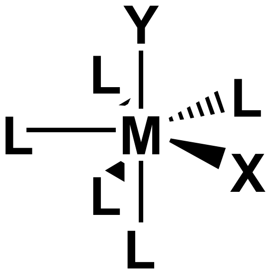
Step 1. Collision of ML_5X with Y to yield a 7-coordinate intermediate. (slow)

$$ML_5X + Y^- \xrightarrow{K_1} [ML_5XY]^-$$

(slow, rate determining)

Capped Octahedron





Pentagonal Bipyramid

Aquation Reactions

Complexes present in solution are susceptible to aquation or hydrolysis.

This means their ligands can be replaced with water
(the opposite of the anation reactions).

As we discussed earlier, even when other ligands are involved, very few reactions proceed without solvent intervention. This complicates the determination of kinetic behavior.

For inert Co(III) complexes it has been found that hydrolysis depends greatly on the pH of the solution.

Acid Hydrolysis of $[Co(NH_3)_5X]^{2+}$

$$[Co(NH_3)_5X]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH_2)]^{3+} + X^-$$

rate = $k_a[Co(NH_3)_5X^{2+}]$ (k_a = acid hydrolysis rate constant, s^{-1})

From the rate law, what mechanism would you predict?

Evidence for the D mechanism:

The rate of aquation follows the bond strength of the Co-X bond; as the bond energy decreases the rate increases.

X =	K_a =
F^-	$9x10^{-8}\ s^{-1}$
Cl^-	$2x10^{-6}\ s^{-1}$
Br^-	$6x10^{-6}\ s^{-1}$
I^-	$8x10^{-6}\ s^{-1}$

$BE_{Co\text{-}X} \downarrow$

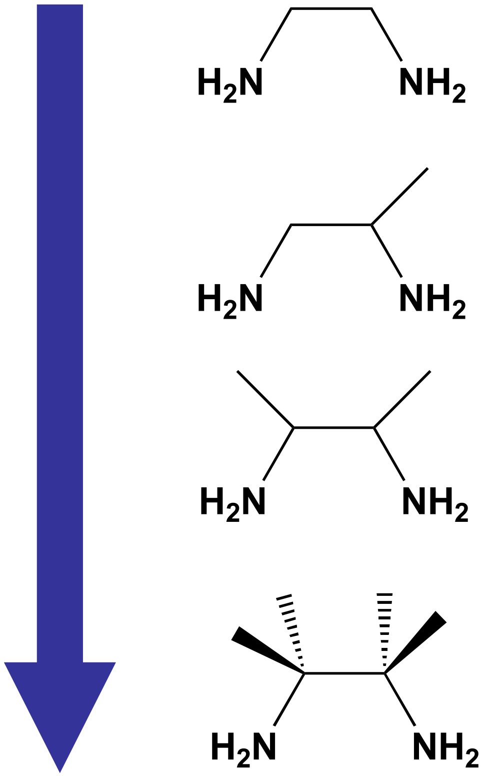
(HSAB theory)

Given K_a is a thermodynamic quantity a larger value means greater stability for $[Co(NH_3)_5(X/L)]^{2+}$and *implies* a stronger bond energy. It is clear that as the Co-X bond energy increases, the (or the k_a for anation increases) K_a for aquation/hydrolysis decreases.

Steric Acceleration of Aquation

As the size of the bidentate ligand in trans-$[Co(N—N)_2Cl_2]^+$ increases, the rate of aquation increases. This is consistent with a dissociatve mechanism as **STERIC CROWDING** weakens the Co-Cl bond.

Increasing bulk



$3.2x10^{-5}$

$6.2x10^{-5}$

$4.2x10^{-3}$

$3.3x10^{-2}$

Charge Effects

A stronger Co-Cl bond in $[Co(NH_3)_5Cl]^{2+}$ results in slower aquation.

$[Co(NH_3)_5Cl]^{2+}$	$[Co(NH_3)_5Cl_2]^{+}$
$6.7x10^{-6}$	$1.8x10^{-3}$

Base Hydrolysis

$$[Co(NH_3)_5X]^{2+} + {}^{-}OH \longrightarrow [Co(NH_3)_5(OH)]^{2+} + X^{-}$$

rate = $k_b[Co(NH_3)_5X^{2+}][OH^-]$ (k_b = base hydrolysis rate constant, $s^{-1}M^{-1}$)

In basic solution, the product of the reaction is the hydroxo complex.

It is found that for this compound k_b is 10^3-10^6 larger than expected.

In fact Co^{3+} complexes are labile toward substitution and decompose to give hydroxides and hydrous metal oxides.

Whys is this reaction so fast?

What does the rate law tell us?

rate = $k_b[Co(NH_3)_5X^{2+}][OH^-]$

BUT……?

There are many anomalous observations to the contrary:

1. OH^- is unique in accelerating the hydrolysis (I^-, and CN^- don't)
2. When NH_3 is replaced by NR_3 the rate decreases and the magnitude of K_b is normal.
3. In basic D_2O (^-OD), H exchanges quickly for D.

These observations suggest a *conjugate base mechanism*.

Specifically, $S_{N1}CB$.

$S_{N1}CB$

Step 1.

$$[Co(NH_3)_5Cl]^{2+} + {}^{-}OH \overset{K}{\longleftrightarrow} [Co(NH_3)_4(NH_2)(Cl)]^{+} + H_2O$$

FAST

Rapid reversible ionization of the complex.
OH^- acts as a base and deprotonates the NH_2-H to give NH_2^- (amido)

THIS IS NOT A RAPID SUBSTITUTION STEP
THIS IS NOT THE RDS

THIS EXPLAINS H/D EXCHANGE

Step 2.

$$[Co(NH_3)_4(NH_2)Cl]^{+} \longrightarrow [Co(NH_3)_4(NH_2)]^{2+} + Cl^{-}$$

Slow RDS

Rate determining step is the loss of Cl- from the amido complex.

(What does the bonding look like?)

This is a dissociative process.
Since the formation of the amido complex is dependent on [$^{-}$OH], the second order rate Law can be understood.

The RDS is very rapid because the amido group is a strong π-donor, it promotes the elimination of Cl^- and the extra l.p. stabilizes the intermediate.

There is also a charge reduction which weakens the Co-Cl bond.

$S_{N1}CB$

Step 3

$[Co(NH_3)_4(NH_2)]^{2+} + H_2O \longrightarrow [Co(NH_3)_5(OH)]^{2+}$ FAST

The overall rate law:

$$\text{rate} = K[Co(NH_3)_4(NH_2)Cl^+]$$

$$= k_2K[Co(NH_3)_5X^{2+}][OH^-]$$

If $k_b = k_2K$ then

$\Big\downarrow$ Agreement with Exp.

$$\text{rate} = k_b[Co(NH_3)_5X^{2+}][OH^-]$$

Reactions of Coordinated Ligands

It is also possible to carry out reactions where ligand exchange does not Involve cleaving the M-L bond. Rather, bonds within the ligands are broken and reformed.

This is seen in the aquation of a carbonato complex in acid solution.

$$[Co(NH_3)_5(OCO_2)]^+ + 2H_3O^+ \longrightarrow [Co(NH_3)_5(OH_2)]^{3+} + 2H_2O + CO_2$$

This is a rapid reaction, something out of character for inert Co^{3+} complexes.

Why?

From experiment with labeled water, there is no label incorporated into the Co coordination sphere.

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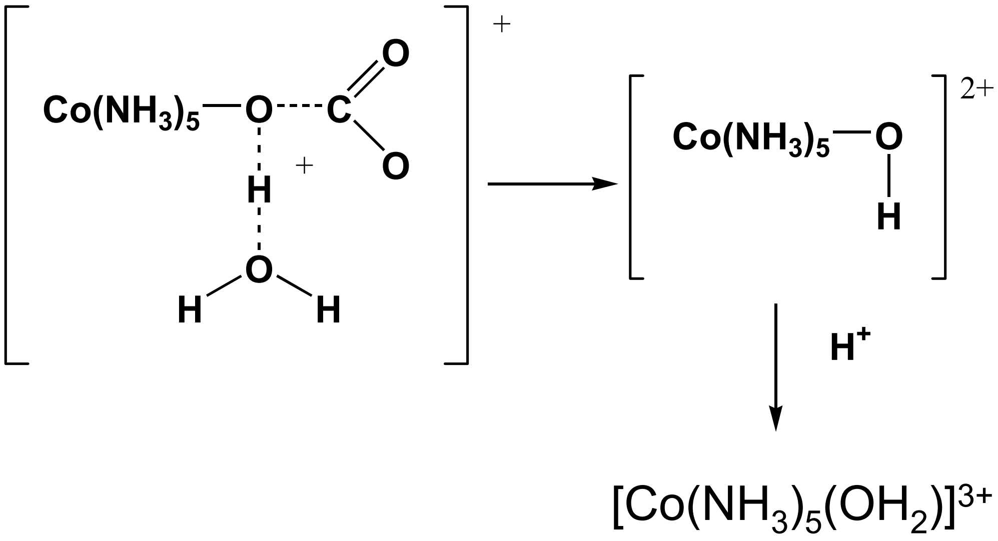
What is happening?

What’s happening?

The most likely path for this reaction involves proton attack on the oxygen of the CO_3^{2-} bonded to the Co.

This attack is followed by the elimination of CO2 and protonation of the hydroxo complex.

THIS IS NOT A SIMPLE SUBSTITUTION OF CO_3^{2-} BY H_2O.



Reactions of 4-Coordinate SP Complexes

Complexes with d^8 electron configurations are usually 4-coordinate and have sqr. planar geometry.

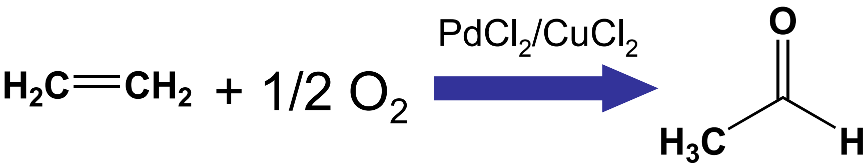
Pt(II), Pd(II), Ni(II) (sometimes tetrahedral, often 6-coordinate, octahedral)
Ir(I), Rh(I), Co(I), Au(III)

Pt(II) has been studied a lot. Its complexes are stable, easy to synthesize and undergo ligand exchange reactions at rates slow enough to allow easy monitoring.

Other d^8 systems react much faster (10^5-10^7x) and the data on these systems is limited.

Current knowledge of SP substitution reactions stems from studies in the 1960s and 70s.

Wacker process. Industrial conversion of ethylene to acetaldehyde.



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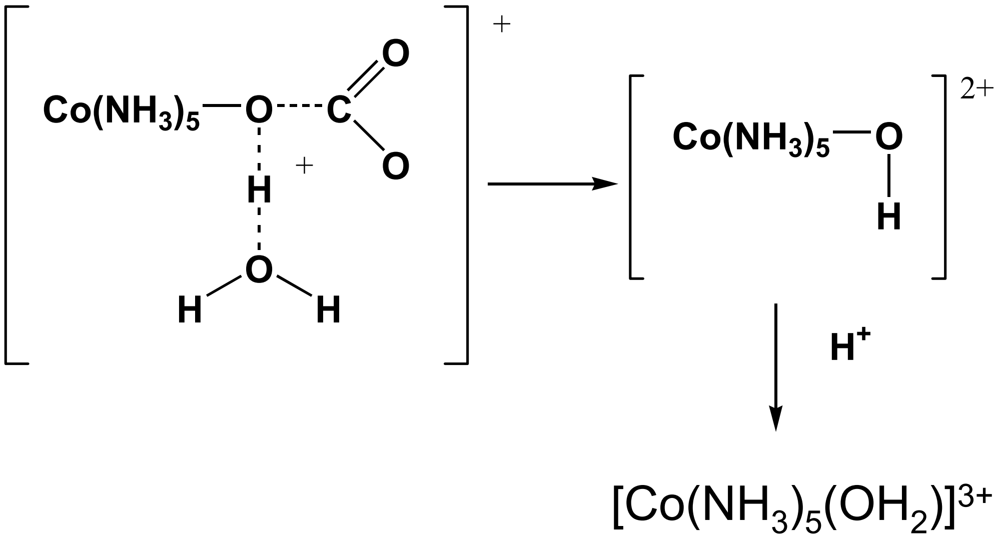

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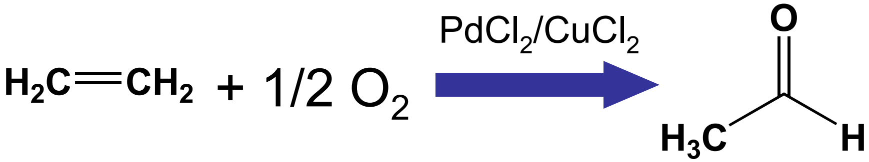
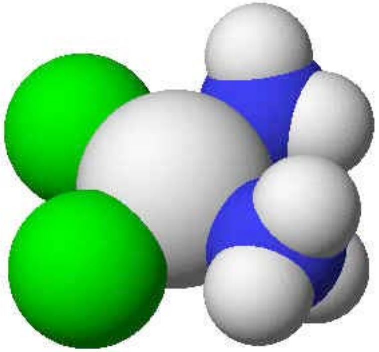
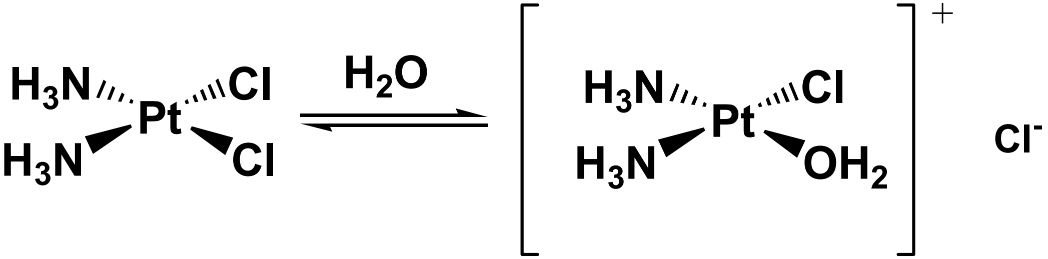


Cis-platin

This is an anti cancer drug which binds to the DNA of cancer cells.

The reversible aquation assists in the transfer of the drug from blood to the tumor where water and Cl- are replaced by the DNA.





Mechanistic Considerations

It is easier to understand mechanisms with 4-coordinate systems than with 6-coordinate octahedral systems as it is expected that S.P. 4-coordinate complexes will be more likely to react via an associative mechanism.

In fact many d^8 systems do react via an S_N2 type mechanism.

For:

$$\mathbf{[PtCl_4]^{2-}, [Pt(NH_3)Cl_3]^{2-}, [Pt(NH_3)_2Cl_2], [Pt(NH_3)\ _2Cl_2]} \xrightarrow{H_2O}$$

Rate constants are almost identical.

This is most readily explained via an associative mechanism.

The General Reaction Pathway

$$[Pt(L)_3X] + Y \longrightarrow [Pt(L)_3Y] + X$$

(L = non-labile ligand, X = L.G., Y= entering ligand)

Rate law. Rate= $k_1[PtL_3X]+k_2[PtL_3X][Y]$

What does this tell you?
How does this differ from every other rate law you have seen?

It indicates that the reaction proceeds via two independent pathways.

The first term…. $k_1[PtL_3X]$

This occurs only when the solvent is a Lewis Base and a potential ligand.

It is believed that this is a two step process involving X being slowing replaced by solvent. The solvent is in turn replaced readily by Y.

$$[Pt(L)_3X] + S \longrightarrow [Pt(L)_3S] + X \quad \text{slow, RDS}$$

$$[Pt(L)_3S] + Y \longrightarrow [Pt(L)_3Y] + S \quad \text{fast}$$

Overall RXN $[Pt(L)_3X] + Y \longrightarrow [Pt(L)_3Y] + X$

The General Reaction Pathway

Solvent Intervention. **Does this look familiar?**

Didn't we say this was an associative mechanism?

Often experimental conditions "mask" the dependence upon [Y].

When a reaction is carried out in a solvent….the solvent is in HUGE excess and it is not necessarily "innocent" (it can take a role in the rxn)

Effectively constant at 55.5M.
Be sure you can determine this!!

Given the excess of water, its concentration remains seemingly constant. As a result, the influence of the water on the mechanism is "masked". This results in a **pseudo-first order rate law**.

Rate Law

Rate = [overall rate] $= k_1[\text{Complex}][H_2O]$
$= \{k_1[H_2O]\}\ [\text{complex}]$
$= K\ [\text{complex}]$

$$\mathbf{[Pt(L)_3X] + S \longrightarrow [Pt(L)_3S] + X}$$ **slow, RDS**

The first term…. **$k_1[PtL_3X]$**

The General Reaction Pathway

The Second Step

$k_2[PtL_3X][Y]$

$F^-, H_2O < Cl^- < NH_3 < py < Br^- < I^- < {}^-SCN < CN^- < PR_3$

increasing k_2 →

Strongly dependent upon Y.

This sequence is the “Nucleophilicity Sequence” for Pt(II).

Generally, Pt(II) prefers soft, polarizable ligands. Recall it is a soft Lewis acid (large, low valent metal ion See HSAB)

What does this tell you about the mechanism?

Step 1. Collision of **PtL_3X** *with Y to yield a 5-coordinate intermediate. (slow)*

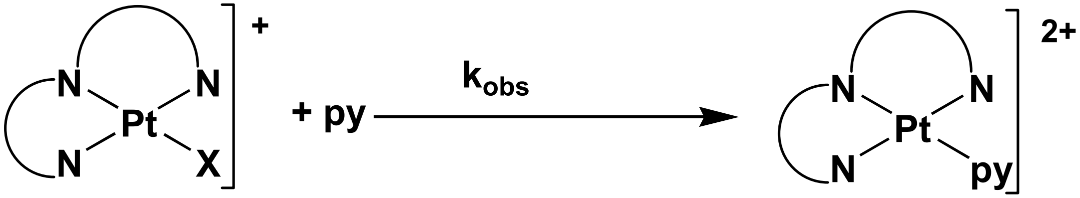
$$PtL_3X + Y \xrightarrow{k_2} PtL_3XY$$ (slow, rate determining)

The General Reaction Pathway

The leaving group should also influence the rate…and k_2.

It is noted that the order of ligands is nearly the reverse of the Nu Series.

Hard ligands (NO_3^-, H_2O) leaving easily and quickly.
Soft ligands (CN^-, ^-SCN) leaving reluctantly.



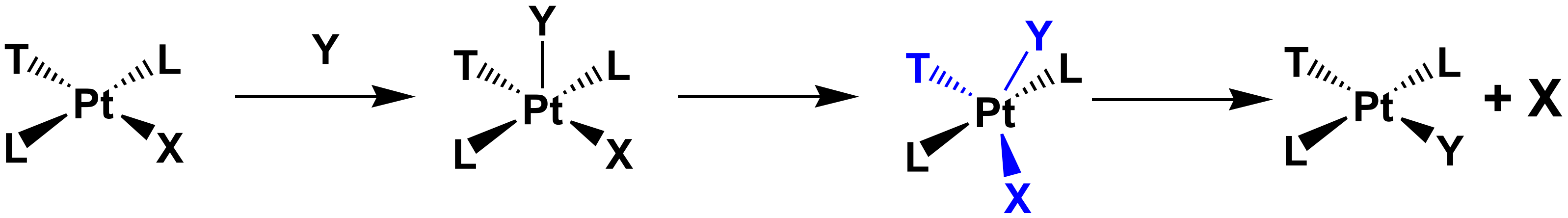
F^-, H_2O < Cl^- < NH_3 < py < Br^- < I^- < ^-SCN < CN^- < PR_3

k_{obs} ($s^{-1}M^{-1}$)	X^-
1.9×10^{-3}	H_2O
3.5×10^{-5}	Cl^-
1.7×10^{-8}	CN^-

Stereochemistry

In the majority of reactions, substitution at the Pt(II) center proceeds with retention of the stereochemistry.

This means that the incoming Y replaces the outgoing X.



1. The entering Y approaches from one side of the plane.
2. Formation of a tbp intermediate via a sp (**TYX** are in the eq plane, **Ls** are in the axial positions). This maintains the trans position of the two L ligands and elimination of X gives the new product with the same stereochemistry.

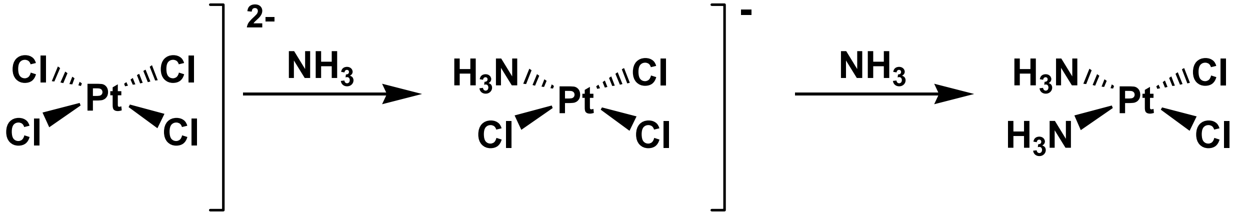
trans- effect.

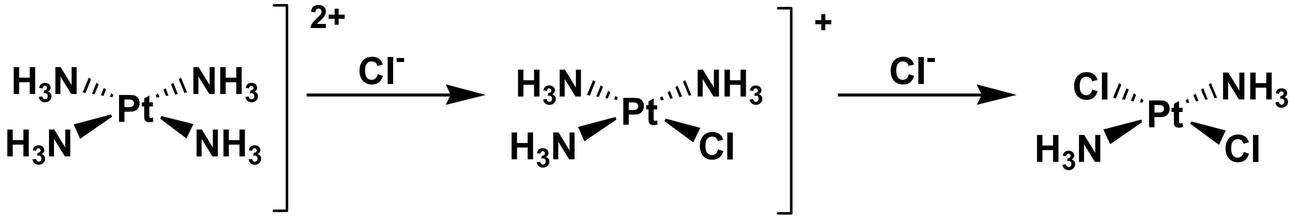
This observation is particularly true for Pt(II) complexes.

The ligand trans to the “leaving” ligand can alter the rate of exchange by orders of magnitude.

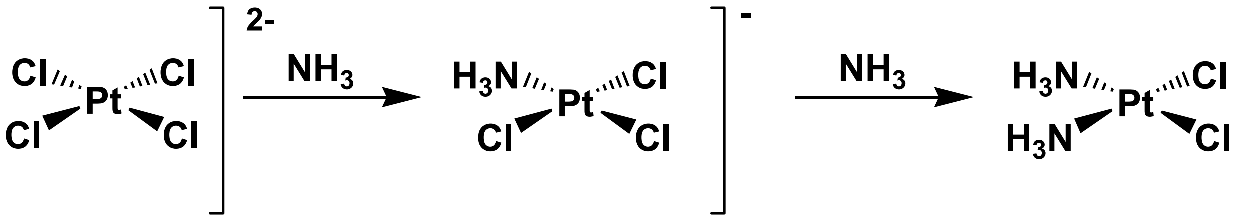
The rich Pt deposits in Russia saw the development of many intensive studies into Pt coordination chemistry. The first stereospecific ligand displacement reactions were discovered.

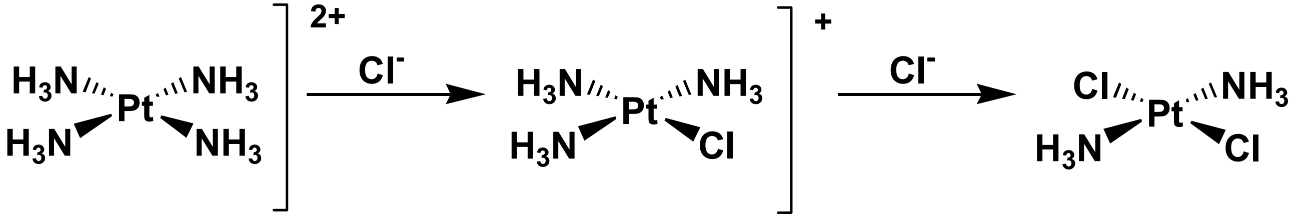
In 1926 Chernyaev introduced the trans effect.





trans-effect





How do we understand this?

Step 1. Simple displacement….all the groups on the starting material are the same. Only one compound forms.

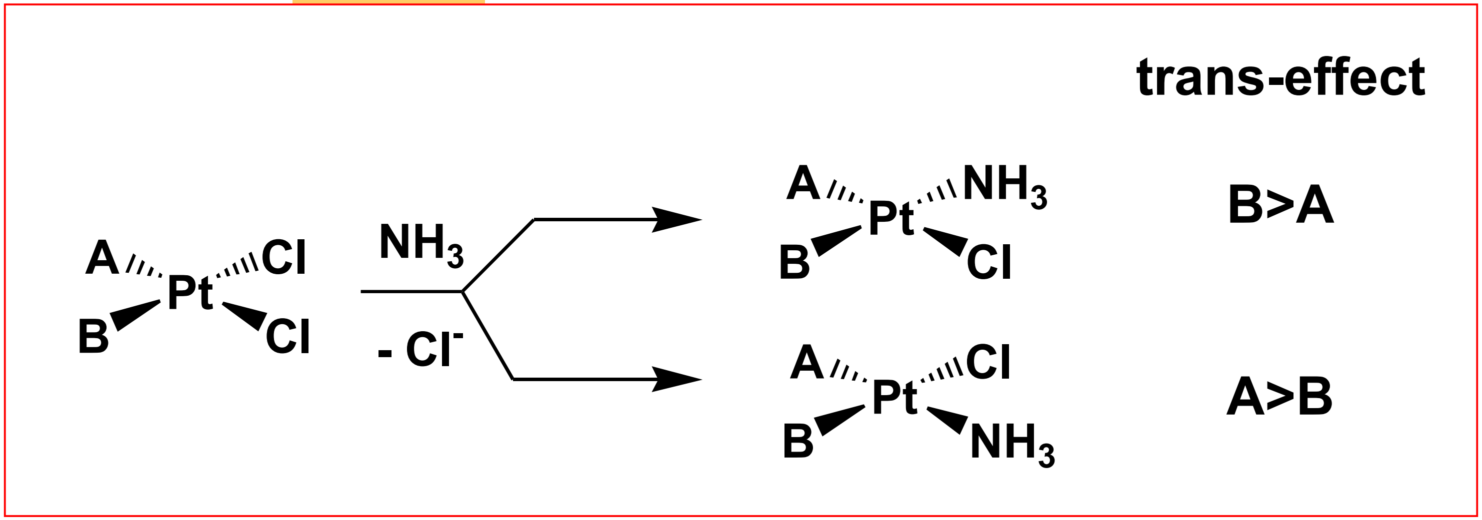
Step 2. Two products can form BUT only one does. Note that in each case the observed isomer arises from the substitution of a ligand trans to to a Cl.

trans-effect

The trans-effect is defined:

“The ability of a ligand to promote rapid substitution of a ligand trans to itself.”

Is this a kinetic or thermodynamic phenomenon?

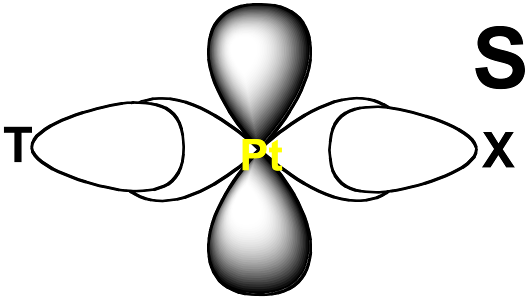


The general order of ligand trans-effect is

$H_2O, OH^- < NH_3, py < Cl^- < Br^- < I^- < {}^-SCN, NO_2^- < C_6H_5 < CH_3^-, SR_2 < H^-, PR_3 < H_2C{=}CH_2, CN^-, CO$

Things to think about…

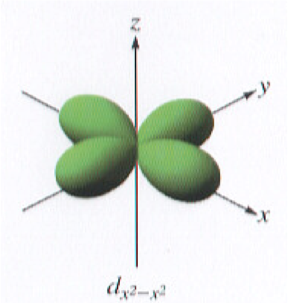
This is a kinetic effect, it depends on activation energies, stabilities of ground state and transition state is relevant.

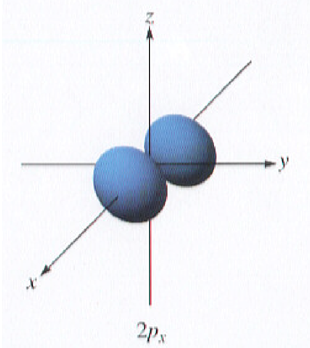


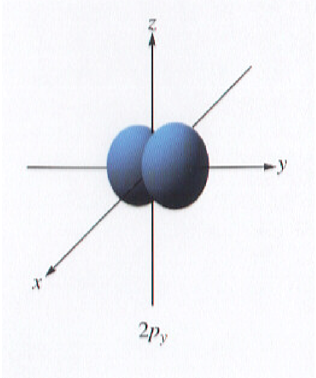
Sigma Bonding Effect

How can the Pt-T bond weaken the trans Pt-X bond?

Molecular orbital calculations hold the answer.







Both the Pt-X and Pt-T bonds involve the d_{x2-y2} and p_x (p_y) orbitals to form sigma bonds.

In the case of a VERY STRONG Pt-σ-bond, there is good overlap between the ligand orbitals and these Pt orbitals.

THIS IS A FANCY WAY TO SAY THAT THE ORBITALS ARE USED UP BY THE STRONG BOND and there is less of the Pt orbitals available for other bonding.

Given the weaker Pt-X bond, its ground state (σ-bonding orbital) is higher energy…….

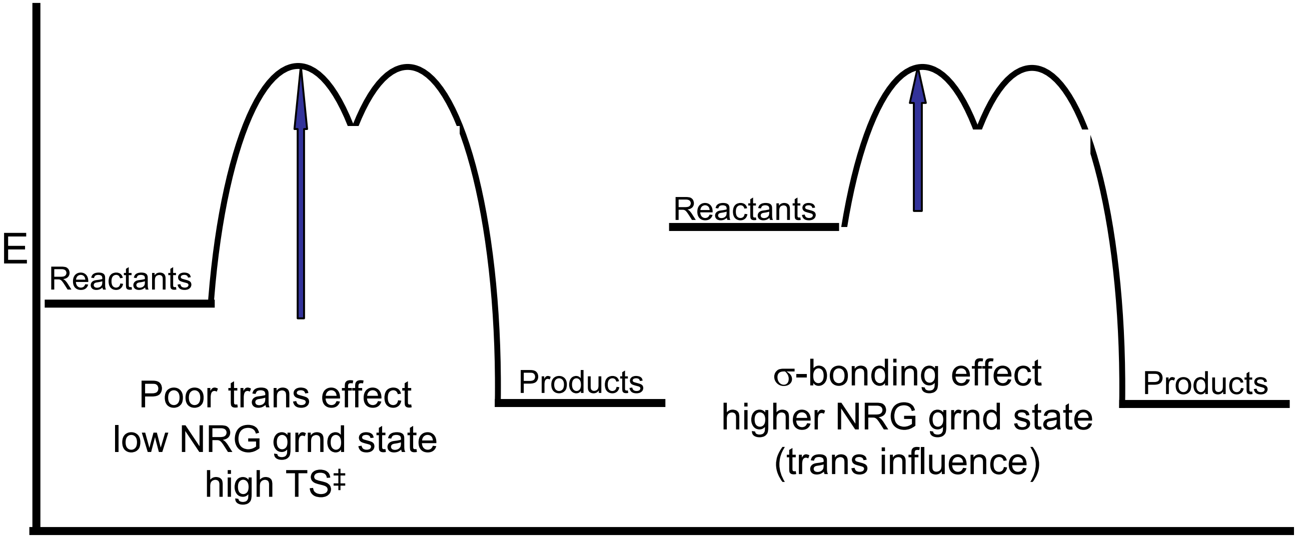
Pt-X Bond and Activation Energy

Given the weaker Pt-X bond, its ground state (σ-bonding orbital) is higher energy leading to a lower activation energy.

This is a thermodynamic effect and influences the kinetics of the reaction by changing the G.S..

The trans-ligand is labilized in an associative mechanism.

influence of ligands follows the σ-ability of ligands. $(H^-, R^- >> {}^-SCN > I^- > Cl^- > NH_3 > OH_2)$



Poor trans effect
low NRG grnd state
high TS‡

σ-bonding effect
higher NRG grnd state
(trans influence)

What about
CO, $H_2C=CH_2$ and PR_3?

Summary of trans effect

1. The highest trans effect is seen for strong π-acceptors followed by strong σ-donors.
2. Ligands at the low end of the series have neither strong σ-donating abilities or π-accepting abilities. **This makes BOTH GS and TS important.**

Propose how to prepare cis-/trans-$[Pt(NH_3)(NO_2)Cl_2]^-$.

Start with?

The general order of ligand trans-effect is

H_2O, OH^-<NH_3,py<Cl^-<Br^-<I^-<$^-$SCN, NO_2^-<C_6H_5<CH_3^-,SR_2<H^-,PR_3<$H_2C=CH_2$,CN^-,CO

Group 4: Ti, Zr, Hf

The discovery of titanium in 1791 is attributed to William Gregor, a Cornish vicar and amateur chemist. He isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4.
Named after the "*Titans*", (the sons of the Earth goddess in Greek mythology)

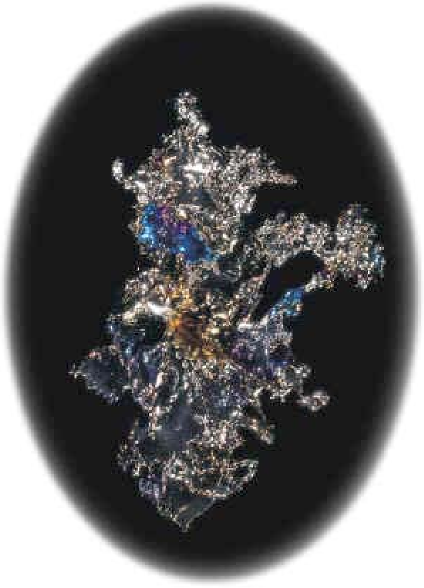
Ti A silver-white metal, known for its hardness, low density (4.5g cm^{-3})
Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction because of its:

Excellent Corrosion Resistance, High Heat Transfer Efficiency
Superior Strength-To-Weight Ratio

When it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.

Although a biological function in man is not known, it has excellent biocompatibility --that is the ability to be ignored by the human body's immune system--and an extreme resistance to corrosion.
Titanium is now the metal of choice for hip and knee replacements.
It is used in military aircraft, nuclear submarines, areas where cost is not really a concern.

Other applications include: MAC TiBooks, golf clubs, bicycles.

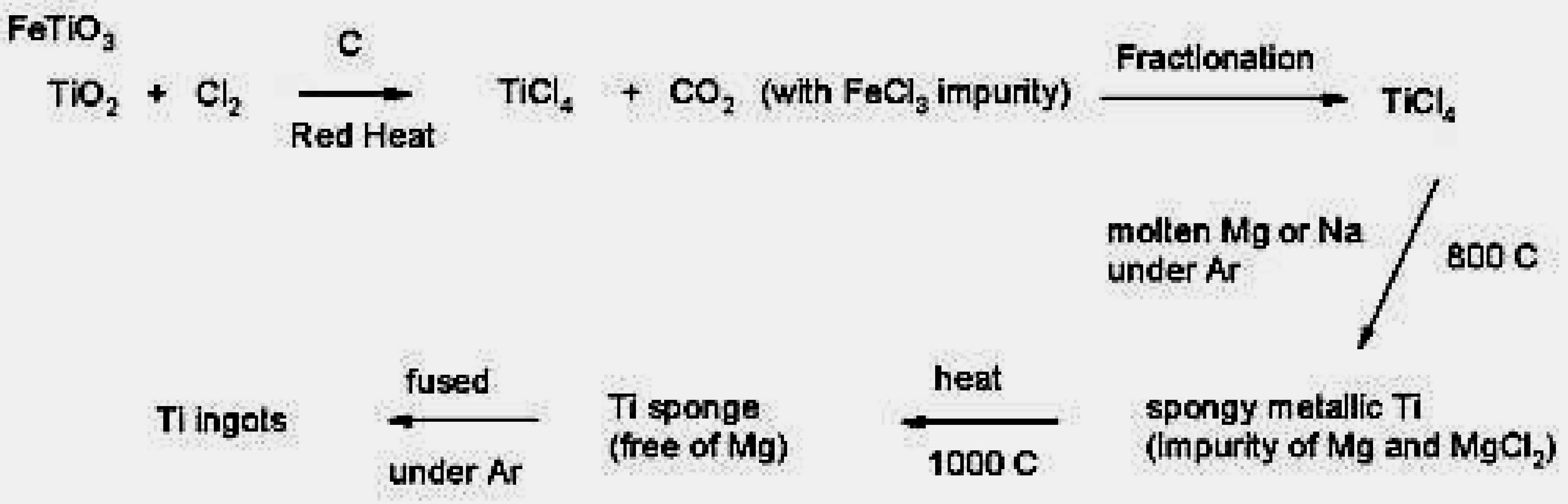


Isolation of Ti

The most common form of Ti in the terrasphere is TiO_2
This is a white solid often used in paint as well as as a “sunshield”.

Kroll allows isolation of Ti.

Conversion to $TiCl_4$……..and reduction to Ti with Mg



Kroll process

Reactions of Ti

Reaction of titanium with air

Titanium metal is coated with a passivating oxide layer that usually renders it inactive. (This is similar to Al and Si)

However once titanium starts to burn in air it burns with a spectacular white flame to form titanium dioxide, TiO_2 and titanium nitride, TiN. Titanium metal even burns in pure nitrogen to form titanium nitride.

$$Ti_{(s)} + O_{2(g)} \rightarrow TiO_{2(s)}$$

$$2Ti_{(s)} + N_{2(g)} \rightarrow TiN_{(s)}$$

Reaction of titanium with water

Titanium will react with steam and form the dioxide, titanium(IV) oxide, TiO_2, and hydrogen, H_2.

$$Ti_{(s)} + 2H_2O_{(g)} \rightarrow TiO_{2(s)} + 2H_{2(g)}$$

Reaction of titanium with the halogens

Titanium does react with halogens upon warming to form titanium(IV) halides. The reaction with fluorine requires heating to 200°C.

$$Ti(s) + 2F_{2(g)} \rightarrow TiF_{4(s)} \text{ [white]}$$

$$Ti(s) + 2Cl_{2(g)} \rightarrow TiCl_{4(l)} \text{ [colourless]}$$

$$Ti(s) + 2Br_{2(g)} \rightarrow TiBr_{4(s)} \text{ [orange]}$$

$$Ti(s) + 2I_{2(g)} \rightarrow TiI_{4(s)} \text{ [dark brown]}$$

Reaction of titanium with acids

Dilute aqueous hydrofluoric acid, HF, reacts with titanium to form the complex anion $[TiF_6]^{3-}$ together with hydrogen, H_2.

$$2Ti_{(s)} + 12HF_{(aq)} \rightarrow 2[TiF_6]^{3-}{}_{(aq)} + 3H_{2(g)} + 6H^+{}_{(aq)}$$

Titanium metal does not react with mineral acids at ambient temperature **but does react with hot hydrochloric acid to form titanium(III) complexes.**

Reaction of titanium with bases

Titanium does not react with bases under normal conditions, even when hot.

A dramatic demonstration of a Ti reaction.

$Ti_{(s)} + KClO_4 \rightarrow TiO_{2(s)} + KCl_{(s)}$ + energy

A few examples of Ti applications.

Hip implants

Golf Clubs

Aircraft

Zirconium

Zirconium is a greyish-white lustrous metal.
Finely divided metal can ignite spontaneously in air, at elevated T.
(The solid metal is much more difficult to ignite.)
The inherent toxicity of zirconium compounds is low.

Ores are mined in a number of countries including Australia, Brazil, India, South Africa and the USA.

Isolation

The Kroll method is also used for zirconium and involves the reaction of chlorine and carbon upon baddeleyite (ZrO_2).

Zirconium tetrachloride, $ZrCl_4$, is separated from the iron trichloride, $FeCl_3$, by fractional distillation.

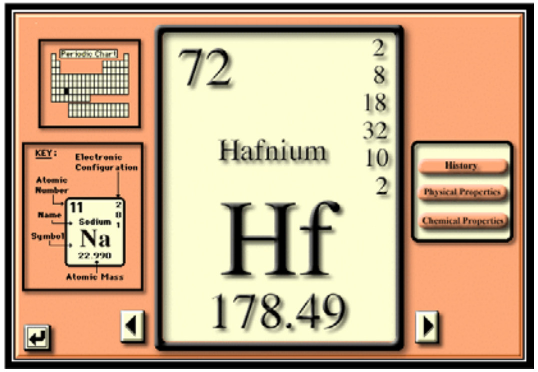
Finally $ZrCl_4$ is reduced to metallic zirconium by reduction with magnesium, Mg. Air is excluded so as to prevent contamination of the product with oxygen or nitrogen.

$$ZrO_2 + 2Cl_2 + 2C\ (900°C) \rightarrow ZrCl_4 + 2CO$$

$$ZrCl_4 + 2Mg\ (1100°C) \rightarrow 2MgCl_2 + Zr$$

Excess magnesium and magnesium chloride are removed from the product with water and hydrochloric acid to leave a zirconium "sponge". This can be melted under helium by electrical heating.

Hafnium



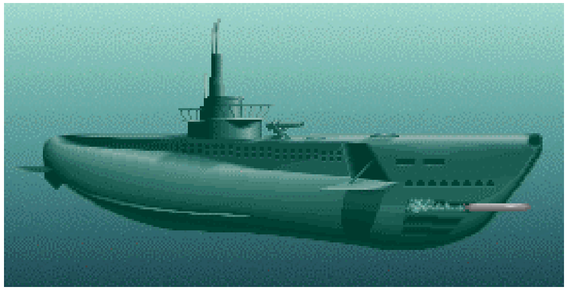
(Hafinia, Latin name for Copenhagen) Many years before its discovery in 1932 (credited to D. Coster and G. von Hevesey), Hafnium was thought to be present in various minerals and concentrations.

It was originally separated from zirconium by repeated recrystallization of the double ammonium or potassium fluorides.

Metallic hafnium was first prepared by van Arkel and deBoer by passing the vapor of the tetraiodide over a heated tungsten filament.

Almost all hafnium metal now produced is made by reducing the tetrachloride with magnesium or with sodium (Kroll Process).

Hafnium is resistant to concentrated bases, but at elevated temperatures reacts with oxygen, nitrogen, carbon , boron , sulfur , and silicon . Halogens react to form tetrahalides.



Hafnium is used in:

-alloying with iron, titanium, niobium and other metals.

-nuclear control rods

-scavenging oxygen and nitrogen

-in gas-filled and incandescent lamps.

Group 4: V, Nb, Ta

Discovered in 1803 by Andres Manuel del Rio and Nils Sefström

Named after "*Vanadis*", the goddess of beauty in Scandinavian mythology

The discovery of vanadium was claimed first by Andres Manuel del Rio (a Spanish mineralogist) at Mexico City in 1803.

He prepared a number of salts from a material contained in "brown lead" (now called vanadite, from a mine near Hidalgo in Northern Mexico). He found the colours reminiscent of those shown by chromium, so he called the element panchromium ("something which can take or have any colour"). He later renamed the element erythronium ("red") after noting that most of these salts turned red upon heating.

It seems he withdrew his claim after a Frenchman, Collett-Desotils, disputed. It was only 30 years later that it was shown that del Rio's work was, in fact, correct.

Metallic vanadium was not made until 1867 when Henry Enfield Roscoe reduced vanadium chloride (VCl_3) with hydrogen gas to give vanadium metal and HCl.

Vanadium Applications

Vanadium metal is important in a number of areas.

Its structural strength and neutron cross section properties makes it useful in nuclear applications.

The metal is used for producing rust-resistant springs and steels used for making tools.

About 80% of the vanadium now produced is used as ferrovanadium or as a steel additive.

75,000
Vanadium Steel
Ford Model T Cars
for 1912

Vanadium foil is used as a bonding agent in binding titanium to steel

The pentoxide V_2O_5 is used in ceramics and as a chemical catalyst.

Vanadium compounds are used for dyeing and printing fabrics.

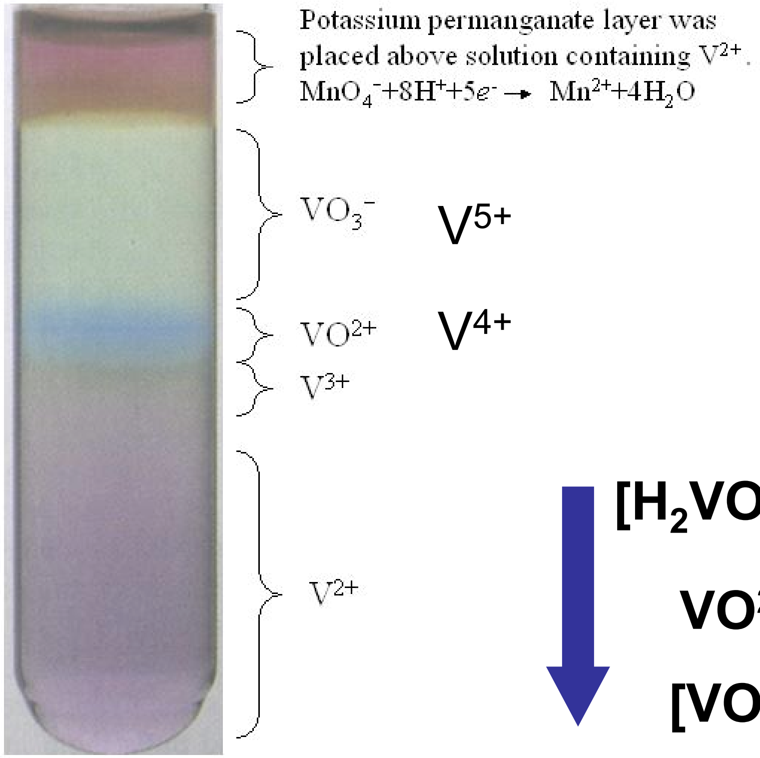
A vanadium-gallium mixture is used in producing superconductive magnets.

Vanadium Chemistry

Redox Chemistry

Readily exists in four different oxidation states d^{0-3}

Oxidation states of vanadium



The same series of colours can be obtained using Zn metal as a reagent.

How does this reaction differ from the $KMnO_4$ reaction?

$$[H_2VO_4]^-_{(aq)} + 4H^+ + e^- \rightarrow VO^{2+}_{(aq)} + 3H_2O_{(l)}$$

$$VO^{2+}_{(aq)} + 4H^+ + e^- \rightarrow V^{3+}_{(aq)} + H_2O_{(l)}$$

$$[VO(OH_2)_5]^{2+}_{(aq)} + e^- \rightarrow [V(OH_2)_6]^{2+}_{(aq)}$$

Exposure of the final solution to air results in reoxidation to V^{3+}.

Biological role

Vanadium is essential to sea squirts (ascidians). The concentration of vanadium in sea squirts is a million times higher than in sea water as a consequence of their ability to concentrate vanadium.

Vanadium is a necessary part of the diet of rats and chicks, but only is very small amounts. Deficiencies cause reduced growth and impair reproduction.

Reaction of vanadium with air

Vanadium metal reacts with excess oxygen, O_2, upon heating to form vanadium(V) oxide, V_2O_5.

$$4V_{(s)} + 5O_{2(g)} \rightarrow 2V_2O_{5(s)} \text{ [yellow-orange]}$$

Reaction of vanadium with water

The surface of vanadium metal is protected by an oxide layer and does not reacts with water under normal conditions.

Reaction of vanadium with the halogens

Vanadium reacts with fluorine, F_2 upon warming to form vanadium(V) fluoride. The other vanadium pentahalides are unknown.

$$2V_{(s)} + 5F_{2(g)} \rightarrow 2VF_{5(l)} \text{ [colourless]}$$

Reaction of vanadium with acids and bases

Vanadium metal is resistant to attack by molten alkali.

Niobium

From the Greek word "*Niobe*" meaning "*daughter of Tantalus*" (tantalum is closely related to niobium in the periodic table)

Discovered in 1801 in England by Charles Hatchett

A mineral (columbite) was sent to England in the 1750s by John Winthrop the Younger, the first goveror of Connecticut, USA.

Hatchett called the new element columbium.

Yet, he was not able to isolate the free element. There was then considerable confusion concerning the distinction between niobium and tantalum as they are so closely related.

This confusion was resolved by Heinrich Rose, who named niobium, and Marignac in 1846. The name niobium is now used in place of the original name "columbium".

The metal niobium was first prepared in 1864 by Blomstrand, who reduced the chloride by heating it in a hydrogen atmosphere.

Reaction of niobium with air

Niobium does not react with air under normal conditions. The surface of niobium metal is protected by a thin oxide layer.

Reaction of niobium with water

Niobium does not react with water under normal conditions. The surface of niobium metal is protected by a thin oxide layer.

Reaction of niobium with the halogens

Niobium does react with the halogens upon warming to form niobium(V) halides.

$$2Nb_{(s)} + 5F_{2(g)} \rightarrow NbF_{5(s)} \text{ [white]}$$

$$2Nb_{(s)} + 5Cl_{2(g)} \rightarrow NbCl_{5(l)} \text{ [yellow]}$$

$$2Nb_{(s)} + 5Br_{2(g)} \rightarrow NbBr_{5(s)} \text{ [orange]}$$

$$2Nb_{(s)} + 5I_{2(g)} \rightarrow NbI_{5(s)} \text{ [brass coloured]}$$

Reaction of niobium with acids

Niobium appears not to be attacked by many acids at room temperature but does dissolve in hydrofluoric acid, HF, or in a mixture of HF and nitric acid, HNO_3.

Reaction of niobium with bases

Niobium metal is largely resistant to attack by molten alkali but will dissolve slowly.

Uses

It is a component of some stainless steels and also alloys with nonferrous metals. These alloys have good strength and other properties, and are used in pipeline construction.

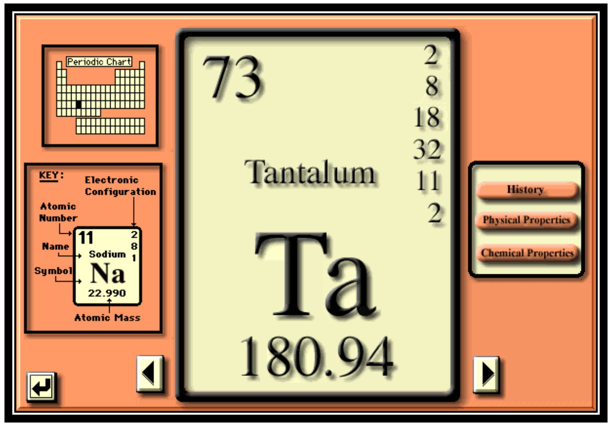
The metal has a low capture crosssection for thermal neutrons and so finds use in the nuclear industries.

The metal is used in arc-welding rods for some grades of stainless steel.

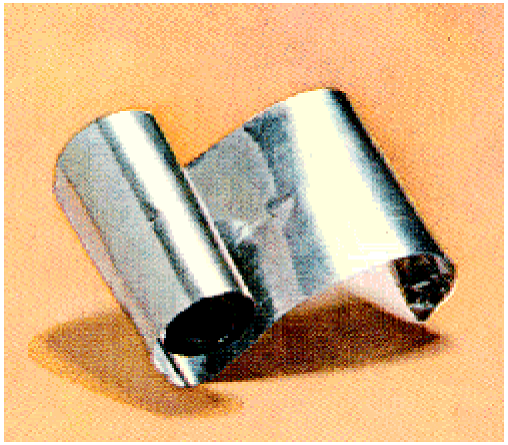
It is used in advanced engineering systems such as those used in the Gemini space program.

Some magnets contain niobium and superconductive magnets are made with Nb-Zr alloy wire.

Because of its bluish colour, niobium is apparently being used for "body art" products, such as navel rings.



Tantalum



Discovered by Anders Ekeberg in 1802

From the Greek word "*Tantalos*" meaning "*father of Niobe*" (Greek mythology, **tantalum** is closely related to **niobium** in the periodic table)

In 1802 many chemists thought niobium and tantalum were the same same element. Primarily because of their chemical similarity. There was some question if perhaps tantalum was an allotrope of niobium.

Proof of the different elements arose when Rose, in 1844, and Marignac, in 1866, demonstrated that niobic and tantalic acids were different.

The first relatively pure tantalum was produced by von Bolton in 1907.

Isolation of Ta

Isolation of tantalum appears is complicated.

Tantalum minerals usually contain both niobium and tantalum.

The similar chemical behavior of these two elements makes them difficult to separate.

Tantalum is extracted from the ores by first fusing the ore with alkali, and then extracting the resultant mixture into hydrofluoric acid, HF.

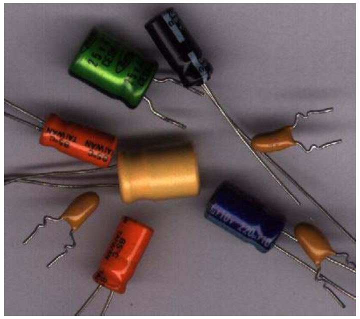
Current methodology involves the separation of tantalum from these acid solutions using a liquid-liquid extraction technique. In this process tantalum salts are extracted into the ketone MIBK (methyl isobutyl ketone, 4-methyl pentan-2-one). The niobium remains in the HF solution. This solvent extraction procedure yields 98% pure niobium oxide in one phase and a 99.5% pure tantalum oxide in another.

After conversion to the oxide, metallic tantalum can be made by reduction with sodium or carbon. Electrolysis of molten fluorides is also used.

Applications of Ta

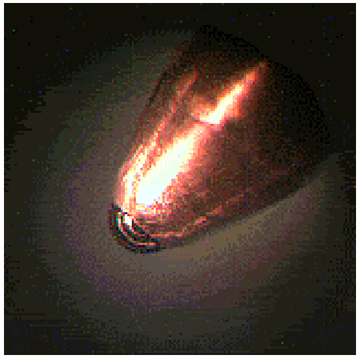
Tantalum is used to make steels with desirable properties such as high melting point, high strength, good ductility. These find use in aircraft and missile manufacture.

It is very inert and so useful in the chemical and nuclear industries to line reactors.



Tantalum wires were those used first for light bulbs (now tungsten is preferred).

The metal is immune to body liquids and the body tolerates the metal well. Therefore, tantalum has widespread use for surgical use. Examples of this include sutures and as cranial repair plates.



The metal is used in the electronics industry for capacitors.

The oxide is used to make special glass with a high index of refraction for camera lenses.

Where does Ta come from?

Tantalum occus in nature in the minerals columbite and tantalite and euxenite.

Niobium and tantalum concentrates are found in Brazil, Canada, Africa, particularly Congo, Australia and Spain.

Tantalum is also obtained as a by product in the extraction of tin from mineral deposits in Malaysia and Nigeria.

Reaction of tantalum with air

Tantalum does not react with air under normal conditions. The surface of tantalum metal is protected by a thin oxide layer.

Reaction of tantalum with water

Tantalum does not react with water under normal conditions. The surface of tantalum metal is protected by a thin oxide layer.

Reaction of tantalum with the halogens

Tantalum does react with the halogens upon warming to form tantalum(V) halides.

$$2Ta_{(s)} + 5F_{2(g)} \rightarrow TaF_{5(s)} \text{ [white]}$$

$$2Ta_{(s)} + 5Cl_{2(g)} \rightarrow TaCl_{5(l)} \text{ [white]}$$

$$2Ta_{(s)} + 5Br_{2(g)} \rightarrow TaBr_{5(s)} \text{ [pale yellow]}$$

$$2Ta_{(s)} + 5I_{2(g)} \rightarrow TaI_{5(s)} \text{ [black]}$$

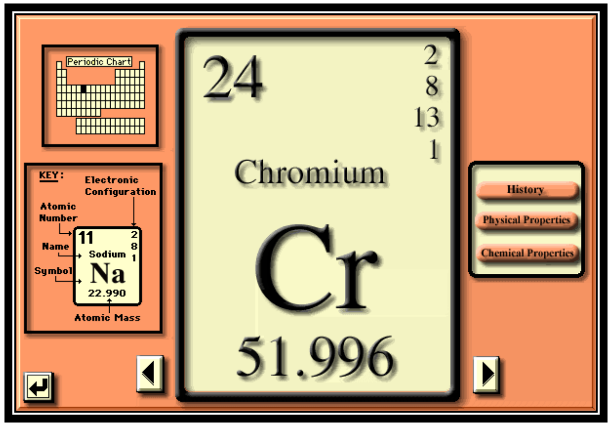
Reaction of tantalum with acids

Tantalum appear not to be attacked by many acids at room temperature but does dissolve in hydrofluoric acid, HF, or oleum (a solution of sulphur trioxide, SO_3, in sulphuric acid, H_2SO_4, also known as fuming sulphuric acid).

Reaction of tantalum with bases

The metal is attacked by molten alkali.

Chromium



Discovered by Louis-Nicholas Vauquelin in France 1797

Chromium is steel-gray, lustrous, hard, metallic, and takes a high polish.

Its compounds are toxic.

It is found as chromite ore.

Siberian red lead (crocoite, $PrCrO_4$) is a chromium ore prized as a red pigment for oil paints.

Gem Stones

Emerald is a form of beryl (a beryllium aluminium silicate) which is green because of the inclusion of a little chromium into the beryl crystal lattice in place of some of the aluminium ions.

Traces of chromium incorporated into the crystal lattice of corundum (crystalline aluminium oxide, Al_2O_3) as a replacement for some of the Al^{3+} ions results in another highly coloured gem stone, in this case the red ruby.

Isolation of Cr

Chromium is not typically prepared in the laboratory given its commercial availability.

The most common commercial source of chromium is the ore chromite, $FeCr_2O_4$.

Oxidation of this ore by air in molten alkali gives sodium chromate, Na_2CrO_4 in which the **chromium is in the +6 oxidation state**. This is converted to the Cr(III) oxide Cr_2O_3 by extraction into water, precipitation, and reduction with carbon. The oxide is then further reduced with aluminium or silicon to form chromium metal.

$$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$$

$$2Cr_2O_3 + 3Si \rightarrow 4Cr + 3SiO_2$$

Another isolation is by electroplating processes. This involves the dissolution of Cr_2O_3 in sulphuric acid to give an electrolyte used for chromium electroplating.

Reaction of chromium with air

Chromium metal does not react with air or oxygen at room temperature.

Reaction of chromium with water

Chromium metal does not react with water at room temperature.

Reaction of chromium with acids

Chromium metal dissolves in dilute hydrochloric acid to form solutions containing the aquated Cr(II) ion together with hydrogen gas, H_2.

In practice, the Cr(II) is present as the complex ion $[Cr(OH_2)_6]^{2+}$. Similar results are seen for sulphuric acid but pure samples of chromium may be resistant to attack. **Chromium metal does not react with nitric acid, HNO_3 and in fact is passivated.**

$$Cr(s) + 2HCl(aq) \quad \rightarrow \quad Cr^{2+}(aq) + 2Cl^{-}(aq) + H_2(g)$$

Cr and halides

Reaction of chromium with the halogens

Chromium reacts directly with fluorine, F_2, at 400°C and 200-300 atmospheres to form chromium(VI) fluoride, CrF_6.

$$Cr(s) + 3F_2(g) \rightarrow CrF_6(s) \text{ [yellow]}$$

Under milder conditions, chromium(V) fluoride, CrF_5, is formed.

$$2Cr(s) + 5F_2(g) \rightarrow 2CrF_5(s) \text{ [red]}$$

Under still milder conditions, chromium metal reacts with the halogens fluorine, F_2, chlorine, Cl_2, bromine, Br_2, and iodine, I_2, to form the corresponding trihalides chromium(III) fluoride, CrF_3, chromium(III) chloride, $CrCl_3$, chromium(III) bromide, $CrBr_3$, or chromium(III) iodide, CrI_3.

$$2Cr(s) + 3F_2(g) \rightarrow 2CrF_3(s) \text{ [green]}$$

$$2Cr(s) + 3Cl_2(g) \rightarrow 2CrCl_3(s) \text{ [red-violet]}$$

$$2Cr(s) + 3Br_2(g) \rightarrow 2CrBr_3(s) \text{ [very dark green]}$$

$$2Cr(s) + 3I_2(g) \rightarrow 2CrI_3(s) \text{ [very dark green]}$$

Where does Cr come from?

Chromium is not found as the free metal in nature.

The most important ore is chromite ($FeCr_2O_4$) and this is found in Turkey, USA, South Africa, Albania, Finland, Iran, Madagascar, Russia, Southern Rhodesia, Transvaal, Cuba, Brazil, Japan, India, Pakistan, and the Philippines.

Crocoite, $PbCrO_4$, is also a chromium mineral and this is found in Russia, Brazil, USA, and Tasmania.

Biology and the Movies

Chromium is an essential trace element and has a role in glucose metabolism. It seems to have an effect in the action of insulin. In anything other than trace amounts, chromium compounds should be regarded as highly toxic.

Erin
Brockovich

Cr(VI)

Industrial prep of dichromate.

We start with a mixed metal oxide: **Chromite $FeCr_2O_4$**.

$$4FeCr_2O_{4\,(s)} + 8Na_2CO_{3(s)} + 7O_2 \longrightarrow 8Na_2CrO_{4\,(s)} + Fe_2O_{3\,(s)} + CO_{2(g)}$$

The addition of water results in LEACHING to leave the iron(III) oxide and a solution of sodium chromate.

To obtain sodium dichromate it is necessary to apply Who's Principle?

$$2Na_2CrO_{4\,(aq)} + 2CO_{2\,(aq)} + H_2O \Longleftrightarrow Na_2Cr_2O_{4(aq)} + 2NaHCO_{3(s)}$$

What does this do?

A little about Cr(VI)

Cr(VI) compounds are thermodynamically unstable BUT kinetic factors lead to several Cr(VI) compounds exisiting.

Chromate $[CrO_4]^{2-}$

This ion exists in neutral and basic conditions

Dichromate $[Cr_2O_7]^{2-}$

This ion exists in acidic conditions

The following equilibrium explains why…

$$2[CrO_4]^{2-}{}_{aq} + 2H^+{}_{(aq)} \leftrightarrow [Cr_2O_7]^{2-}{}_{(aq)} + H_2O_{(l)}$$

The chromate ion is the conj. base of hydrogen chromate….hence it exists in basic solution.

$$[CrO_4]^{2-}{}_{(aq)} + H_2O_{(l)} \leftrightarrow [HCrO_4]^-{}_{(aq)} + OH^-{}_{(aq)}$$

Chromates

Many chromates are insoluble…..

$PbCrO_4$ has a high refractive index, low solubility in water and it is yellow.

What might it be used for?
How can different colours be obtained from this compound….
they can range from red/orange-yellow.

This should worry you……..how can Cr(VI) be coloured?

What is its electron configuration?

The Mohr Method for Cl^- determination

Silver (I) chromate (Ag_2CrO_4) is brick red.

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$$

$$2Ag^+_{(aq)} + [CrO_4]^{2-}_{(aq)} \rightarrow Ag_2CrO_{4(s)}$$

1. Add silver ions to a solution containing Cl^-.
2. When all of the Cl^- is consumed it is very difficult to identify the endpoint. Enter **Ag_2CrO_4!**

At very low concentration of CrO_4^{2-}(~0.01M) the brick red ppt will for indicating the endpoint.

Chromium Applications

To harden steel, to manufacture stainless steel, and to form alloys

Plating to produce a hard, beautiful surface and to prevent corrosion.

Wide use as a catalyst

Dichromates such as K2Cr2O7 are oxidising agents and are used in quantitative analysis and also in tanning leather

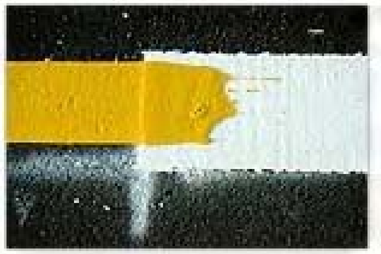
Lead chromate as chrome yellow is a pigment (DCC).

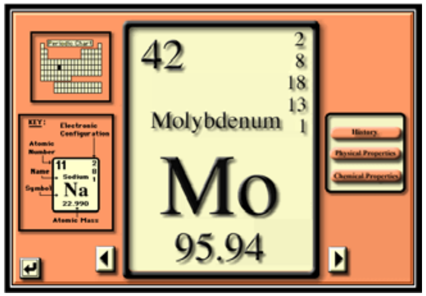
compounds are used in the textile industry as mordants

used by the aircraft and other industries for anodising aluminium

the refractory industry uses chromite for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stable crystalline structure

tanning leather





Molybdenum

Discovered by Carl William Scheele in Sweden 1781.

Isolated from molybdenite.

From the Greek word "molybdos" meaning "lead"

Molybdenum metal was prepared in an impure form in 1782 by Peter Jacob Hjelm.

Molybdenum is not found as the free metal. The main ore is molybdenite (molybdenum sulphide, MoS_2). Molybdenum is recovered as a by-product of copper and tungsten production.

The metal is prepared from the powder made by the hydrogen reduction of purified molybdic trioxide or ammonium molybdate.

Reactions of molybdenum

Air

At room temperature, molybdenum does not react with air or oxygen, O_2. At elevated temperatures (red heat), the trioxide molybdenum(VI) oxide, MoO_3, is formd.

$$2Mo_{(s)} + 3O_{2(g)} \rightarrow 2MoO_{3(s)}$$

Water

At room temperature, molybdenum does not react with water.

Halogens

Molybdenum reacts directly with fluorine, F_2, at room temperature to form molybdenum(VI) fluoride, MoF_6. The conditions are much milder than those required for chromium (immediately above molybdenum in the periodic table).

$$Mo_{(s)} + 3F_{2(g)} \rightarrow MoF_{6(l)} \text{ [colourless]}$$

Under carefully controlled conditions, molybdenum(V) fluoride, MoF_5, is formed in the reaction between molybdenum metal and chlorine, Cl_2.

$$2Mo_{(s)} + 5Cl_{2(g)} \rightarrow 2MoCl_{5(s)} \text{ [black]}$$

Mo uses

valuable alloying agent (contributes to the hardness and toughness of quenched and tempered steels). Almost all ultra-high strength steels contain molybdenum in amounts from 0.25 to 8%

improves the strength of steel at high temperatures

electrodes for electrically heated glass furnaces

nuclear energy applications

missile and aircraft parts

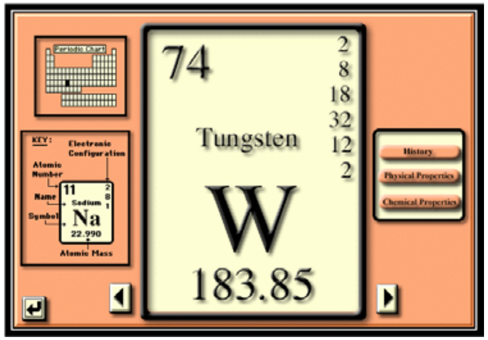
valuable catalyst in petroleum refining

filament material in electrical applications

essential trace element in plant nutrition. Some soils are barren for lack of this element in the soil

molybdenum disulphide is a good lubricant, especially at high temperatures where normal oils decompose

an ancient Japanese sword blade made by Masamuné in 1330 was found to contain molybdenum



Tungsten

Discovered by Fausto and Juan Jose de Elhuyar in Spain 1783

From the Swedish words "*tung sten*" meaning "*heavy stone*" (the origin of the symbol W is "*wolfram* ", named after the tungsten mineral *wolframite*)

Tungsten used to be known as wolfram (from wolframite, said to be named from **wolf rahm** or **spumi lupi**, because the ore interfered with the smelting of tin and was supposed to devour the tin). The de Elhuyar brothers found an acid in wolframite in 1783 that they succeeded in reducing to the elemental metal with charcoal.

Tungsten is found in:
- wolframite (iron-manganese tungstate, $FeWO_4$/$MnWO_4$)
- scheelite (calcium tungstate, $CaWO_4$) ores.

China produces 75% of the world's tungsten.

Reaction of tungsten with air

At room temperature, tungsten does not react with air or oxygen, O_2. At elevated temperatures (red heat), the trioxide tungsten(VI) oxide, WO_3, is formed.

Finely divided tungsten metal is pyrophoric.

$$2W(s) + 3O_2(g) \rightarrow 2WO_3(s)$$

Reaction of tungsten with water

At room temperature, tungsten does not react with water.

Reaction of tungsten with the halogens

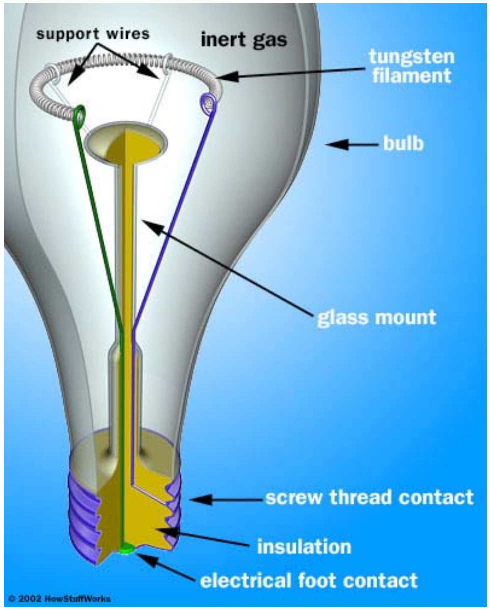
Tungsten reacts directly with fluorine, F_2, at room temperature to form tungsten(VI) fluoride, WF_6. The conditions are much milder than those required for chromium.

$$W(s) + 3F_2(g) \rightarrow WF_6(g) \text{ [colourless]}$$

Tungsten reacts directly with chlorine, Cl_2, at 250°C or bromine, Br_2, to. Under carefully controlled conditions, tungsten(V) chloride, WCl_5, is formed in the reaction between tungsten metal and chlorine, Cl_2.

$$W(s) + 3Cl_2(g) \rightarrow WCl_6(s) \text{ [dark blue]}$$
$$W(s) + 3Br_2(l) \rightarrow WBr_6(s) \text{ [dark blue]}$$
$$2W(s) + 5Cl_2(g) \rightarrow 2WCl_5(s) \text{ [dark green]}$$

Reaction of tungsten with the halogens and the light bulb



A **halogen lamp** also uses a tungsten filament, but it is encased inside a much smaller **quartz envelope**.

I_2 vapor combines with tungsten vapor to form WI_2.
WI_2 redeposits on the filament and decomposes to produce W them on the filament.

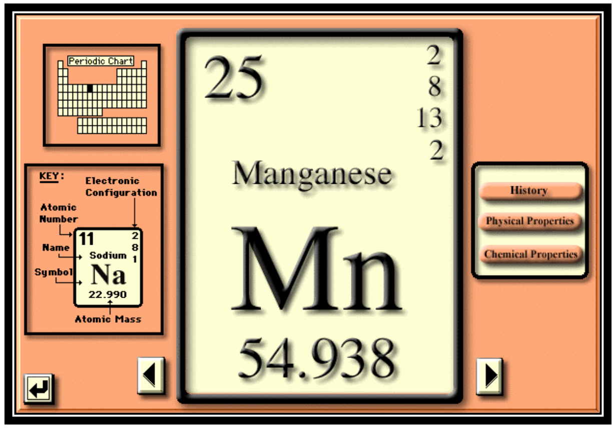
This **recycling** process lets the filament last a lot longer.

Biological role

Tungsten has a limited biological role. A number of enzymes (oxidoreductases) employ tungsten in a way related to molybdenum, (using tungsten.pterin complex). The structure of a tungstoenzyme aldehyde ferredoxin oxidoreductase is known (Protein Data Bank code 1AOR).

W applications

- glass-to-metal seals since the thermal expansion is about the same as borosilicate glass
- tungsten and its alloys are used extensively for filaments for electric lamps, electron and television tubes, and for metal evaporation work
- electrical contact points for car distributors
- X-ray targets
- windings and heating elements for electrical furnaces
- missile and high-temperature applications
- high-speed tool steels
- the carbide is important to the metal-working, mining, and petroleum industries
- calcium and magnesium tungstates are widely used in fluorescent lighting
- tungsten salts are used in the chemical and tanning industries
- tungsten disulphide is a dry, high-temperature lubricant, stable to 500°C
- tungsten bronzes and other tungsten compounds are used in paints



Manganese

Specimen of ore from Cwm Mynach mine

Discovered by Johann Gahn in Sweden (1774)

From the Latin word "*magnes*" meaning "*magnet*", or "*magnesia nigri*" meaning "*black magnesia*" (MnO_2)

Gahn reduced the dioxide (MnO_2, as the mineral pyrolusite) with charcoal (essentially carbon) by heating and the result was a sample of the metal manganese.

Manganese compounds are essential to life. They are essential for the action of some enzymes. Soil deficiencies lead to infertility in mammals and to bone malformation in growing chicks.

Reaction of manganese with air

Manganese is not particularly reactive to air. The surface of manganese lumps oxidize slightly. When finely divided, manganese metal burns in air. It burns in oxygen to form the oxide Mn_3O_4 and in nitrogen to form the nitride Mn_3N_2.

$3Mn(s) + 2O_2(g) \rightarrow Mn_3O_4(s)$

$3Mn(s) + N_2(g) \rightarrow Mn_3N_2(s)$

Reaction of manganese with water

Manganese does not react with water under normal conditions.

Reaction of manganese with the halogens

$Mn(s) + Cl_2(g) \rightarrow MnCl_2(s)$

$Mn(s) + Br_2(g) \rightarrow MnBr_2(s)$

$Mn(s) + I_2(g) \rightarrow MnI_2(s)$

$Mn(s) + F_2(g) \rightarrow MnF_2(s)$

$2Mn(s) + 3F_2(g) \rightarrow 2MnF_3(s)$

Reaction of manganese with acids

Manganese metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated Mn(II) ion together with hydrogen gas, H_2. In practice, the Mn(II) is present as the virtually colourless complex ion $[Mn(OH_2)_6]^{2+}$.

$Mn(s) + H_2SO_4(aq) \rightarrow Mn^{2+}(aq) + SO_4^{2-}(aq) + H_2(g)$

Mn Uses

-used to form many important alloys. In steel, manganese improves the rolling and forging qualities, strength, toughness, stiffness, wear resistance, hardness, and hardenability. With aluminium and antimony, especially with small amounts of copper, it forms highly ferromagnetic alloys. Manganese metal is ferromagnetic only after special treatment

- MNO_2 is used in the preparation of oxygen, chlorine, and in drying black paints
- MNO_2 (pyrolusite) is used as a depolariser in dry cells, and is used to "decolourise" glass that is coloured green by impurities of iron.

Manganese by itself colours glass an amethyst colour, and is responsible for the colour of true amethyst

- important in the utilisation of vitamin B_1
- the permanganate is a powerful oxidising agent and is used in quantitative analysis and in medicine