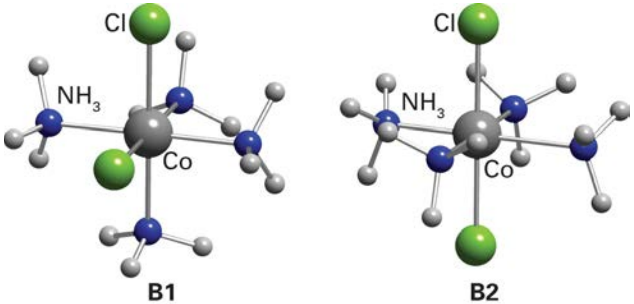
Alfred Werner: Father of Coordination Chemistry.

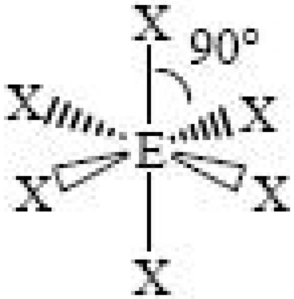
1866-1919
Nobel Prize in Chemistry, 1913

Structure of $Co(NH_3)_6Cl_3$ is NOT $Co(NH_3\text{-}NH_3\text{-}NH_3\text{-}Cl)_3$ but rather is an octahedron with 6 NH_3 directly attached to Co(III) and 3 Cl^- are dissociable counterions, consistent with electrical conductivity of solutions- a 1:3 electrolyte.

If this analysis is correct then the 1:1 electrolyte $[Co(NH_3)_4Cl_2]Cl$ should exist in two isomeric forms. It does; one is green and one is purple.

Transition metals have 2 valencies: their coordination number and their charge balance requirement. The octahedron is a common geometry in coordination chemistry.



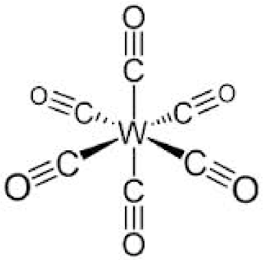
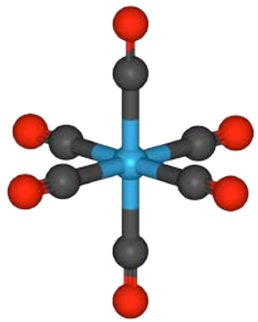
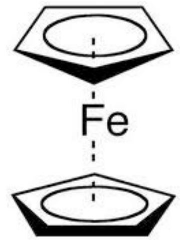
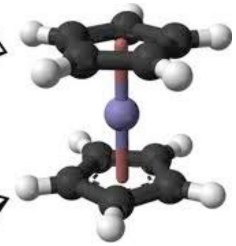
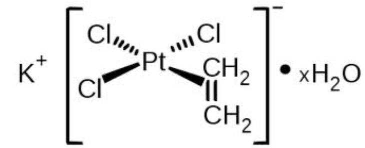
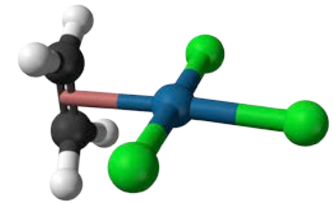


These are real and stable entities. They have thermodynamic stability

Table 7.4 Formation constants of Ni(II) ammines, $[Ni(NH_3)_n(OH_2)_{6-n}]^{2+}$

n	K_f	log K_f	K_n/K_{n-1} Experimental	Statistical*
1	525	2.72		
2	148	2.17	0.28	0.42
3	45.7	1.66	0.31	0.53
4	13.2	1.12	0.29	0.56
5	4.7	0.63	0.35	0.53
6	1.1	0.04	0.23	0.42

* Based on ratios of numbers of ligands available for replacement, with the reaction enthalpy assumed constant.

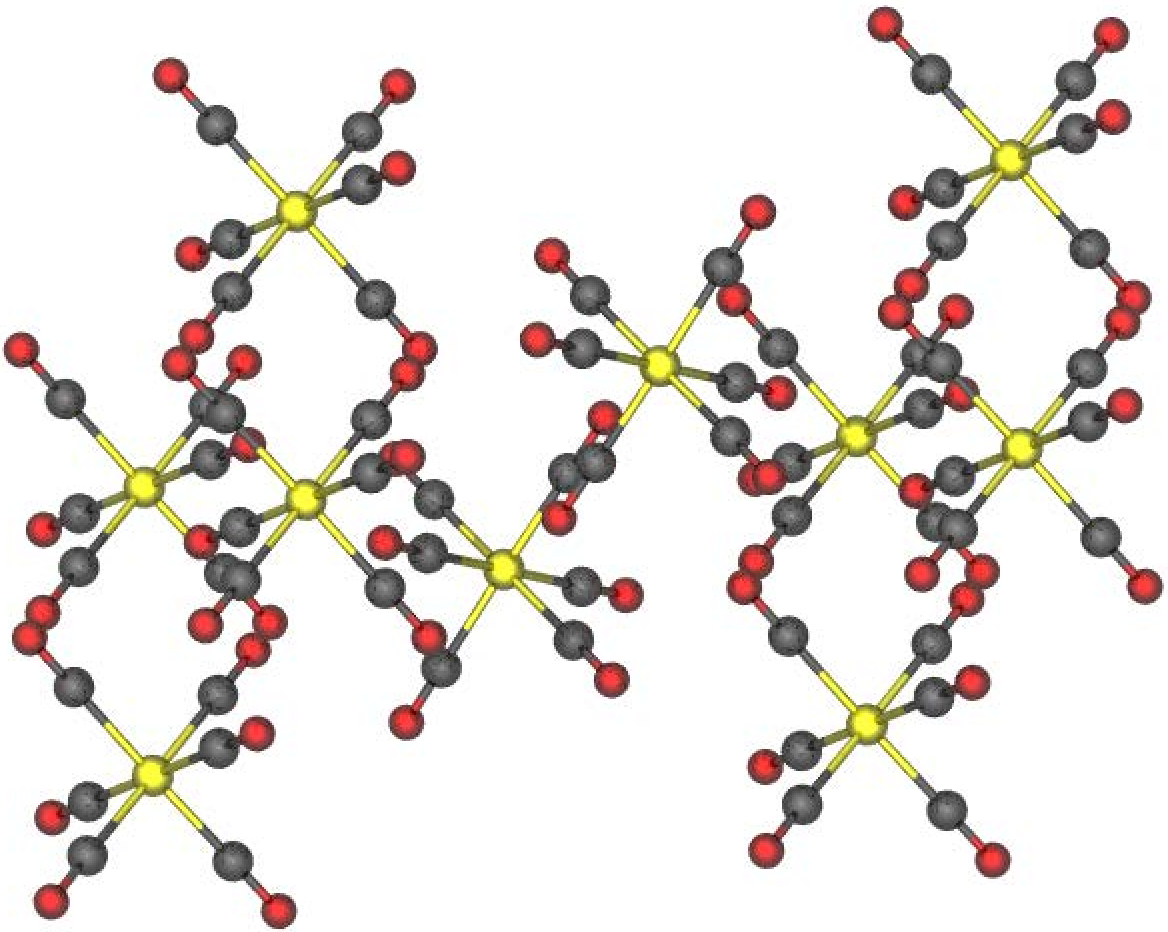
     

Foundation Molecules of Transition Metal Organometallic Chemistry

- Homoleptic Metal Carbonyls
- Ferrocene and Metallocenes
- Zeise's "salt"

Metal Carbonyls: German Chemistry, 1930's

From X-ray crystallography. A portion of a "packing diagram" or the "extended structure" of $W(CO)_6$

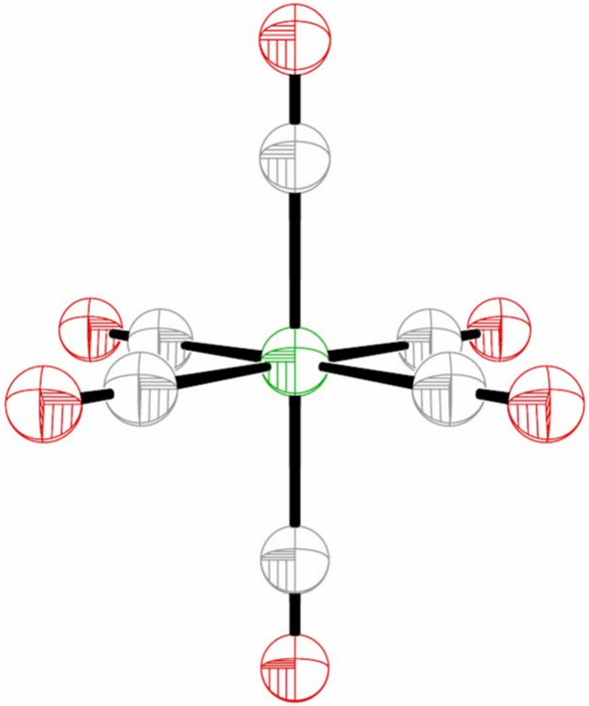


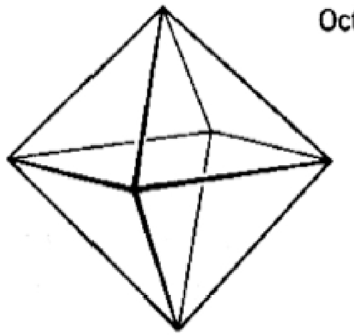
A TEP (Thermal Ellipsoid Plot) of

a single molecule of

tungsten hexacarbonyl, $W(CO)_6$

Thermal ellipsoids indicate extent of
thermal motion. The tighter, rounder the atom, the better the structure. This one looks great.

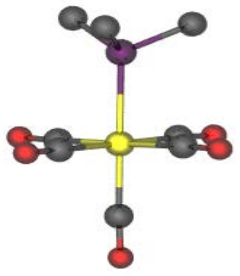




Octahedron
Faces: 8 equilateral triangles
Vertices: 6
Edges: 12

An octahedron has 48 symmetry operations:
E, 8 C_3, 6C_4, 6C_2, I, 6S_4, 8S_6, 3σ_h, 6 σ_d

$W(CO)_6$ + PMe_3 $\xrightarrow{\Delta}$ $W(CO)_5PMe_3$ + CO



Ball and Stick structure of $W(CO)_5(PMe_3)$

NOTE:

- ❖ PMe_3 is placed along the unique (z) axis. What is the order of that axis?
- ❖ Symmetry operations/elements are lost as compared to $W(CO)_6$. What are they?
- ❖ What is the point group assignment?
- ❖ How about multiply substituted complexes:
  - ❖ $W(CO)_4(PMe_3)_2$ => Are there isomers? Point groups?
  - ❖ $W(CO)_3(PMe_3)_3$ => Isomers? Point Group assignments?

What the metal carbonyls have taught us about TM Organometallic Chemistry:

- The Eighteen Electron Rule
- Metal-Metal Bonds
- Clusters
- π – backbonding
- Stabilization of Low Oxidation States
- v(CO) IR and Symmetry
- Ligand Substitution Rxn Mechanisms
- Charge Distribution
- Nucleophilic Attack/Reactivity at CO Ligand
- Conversion of CO to Fischer Carbene
- Applications to Catalysis (as $M(CO)_x$ homoleptic complexes)

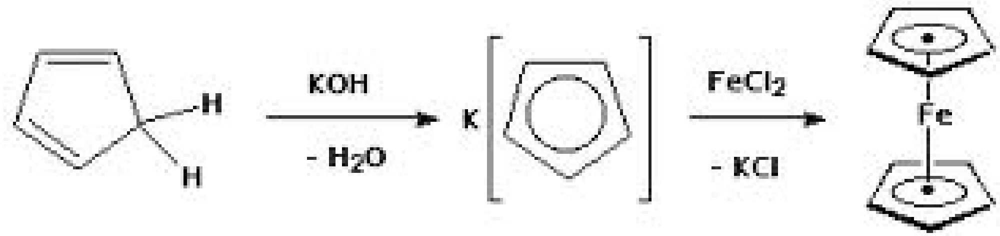
  - Water Gas Shift Reaction

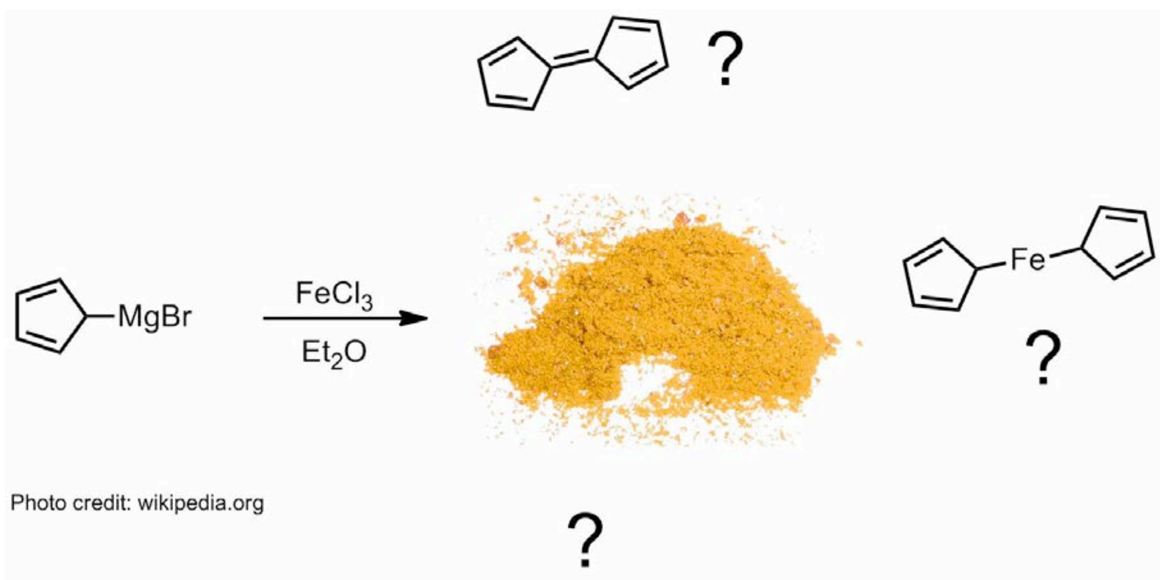
    $$CO + H_2O = CO_2 + H_2$$

  - Hydroformylation

    $$H_2C{=}CH_2 + CO + H_2 \Rightarrow CH_3CH_2CHO$$

Ferrocene: $(\eta^5\text{-}C_5H_5)_2Fe$

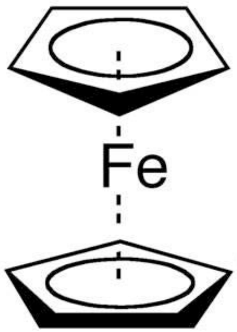


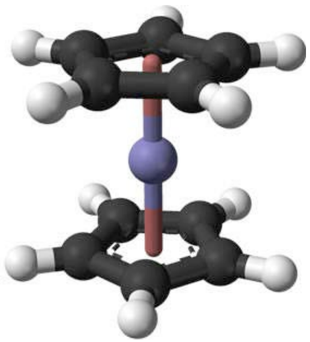


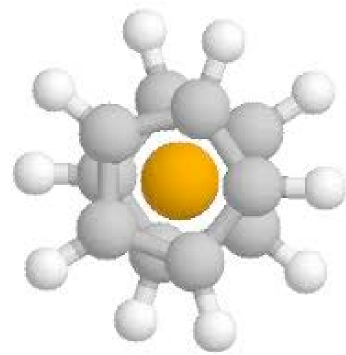
mpt: 172° C; bpt: 250° C !! No decomposition.

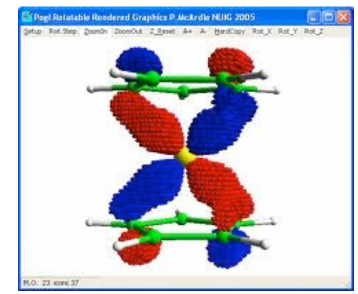
https://www.youtube.com/watch?v=H6_E6C_e_fg

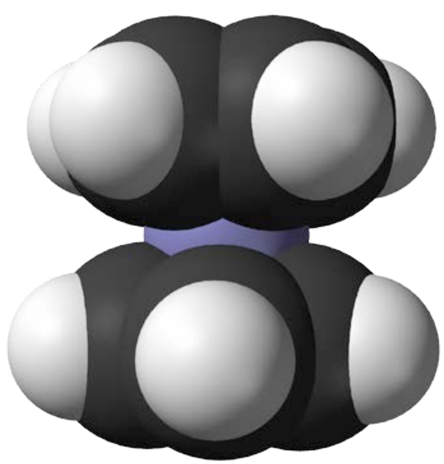
Ferrocene: $(\eta^5\text{-}C_5H_5)_2Fe$

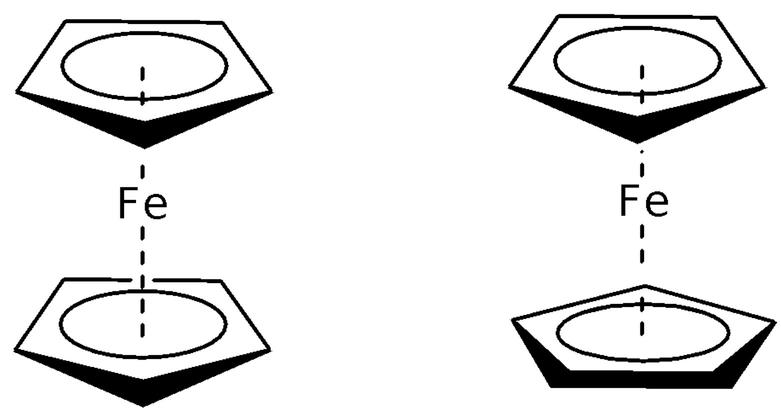






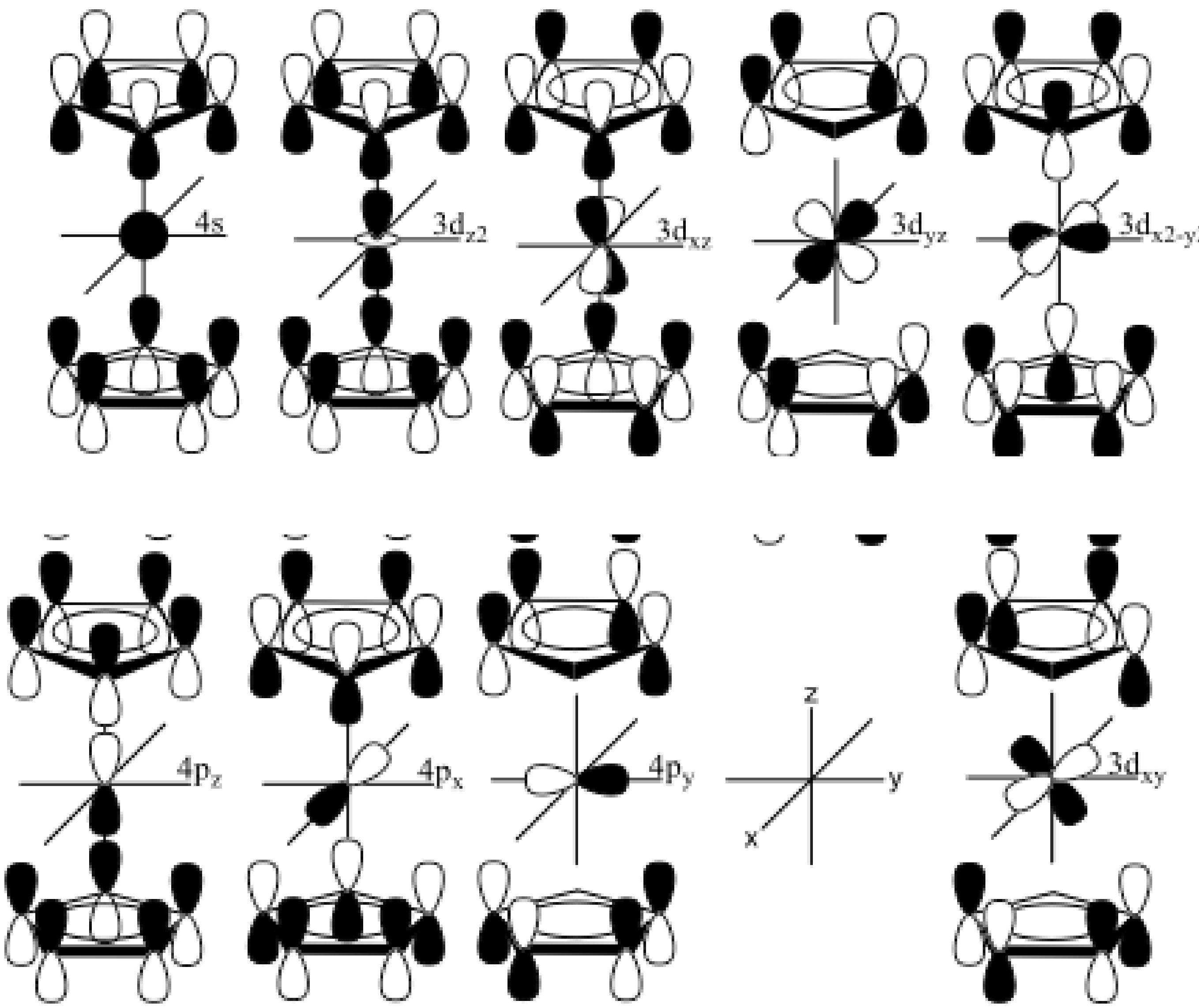




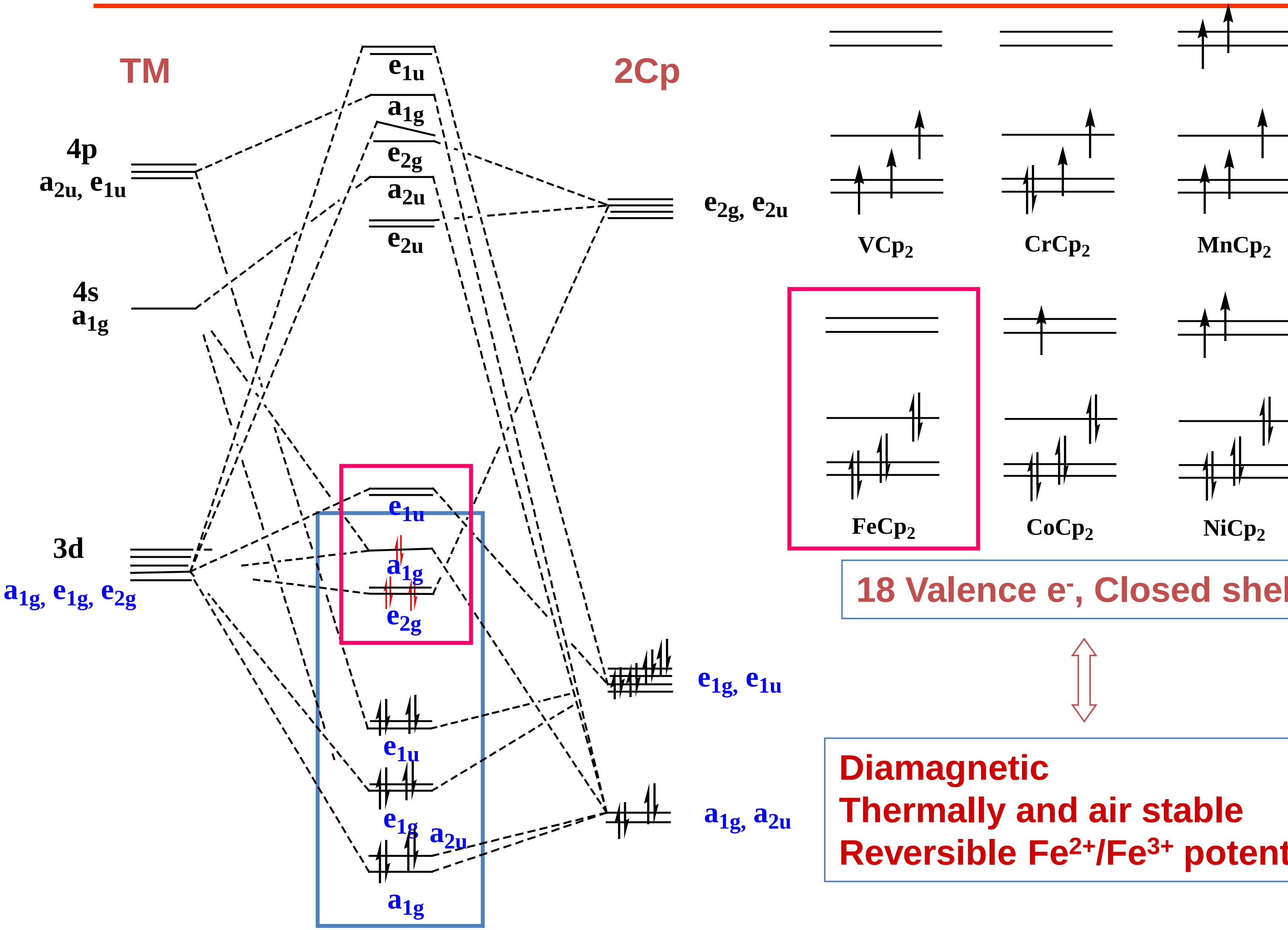


Eclipsed (D_{5h}) Staggered (D_{5d})

Ferrocene: $(\eta^5\text{-}C_5H_5)_2Fe$ Orbital overlap



Electronic structure and properties



18 Valence e$^-$, Closed shell

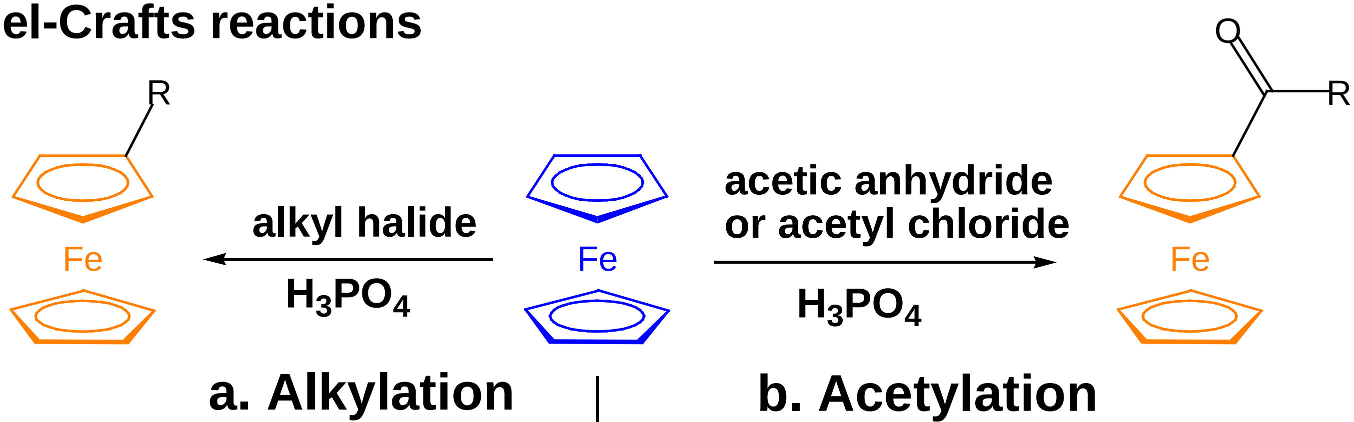
Diamagnetic
Thermally and air stable
Reversible Fe^{2+}/Fe^{3+} potential

http://www.ilpi.com/organomet/cp.html

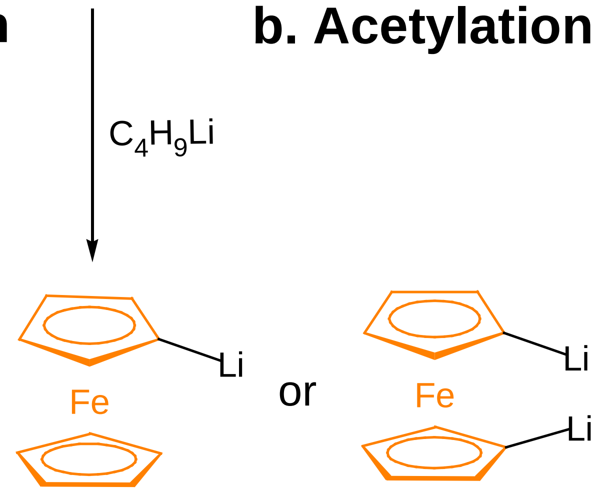
Reactivity of ferrocene

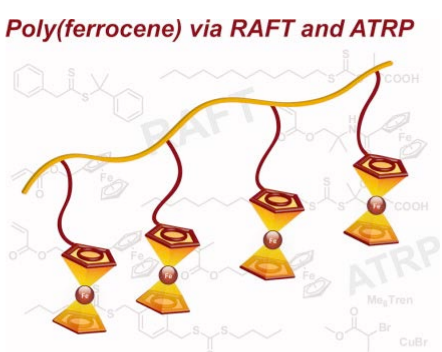
Electrophilic Aromatic Substitution

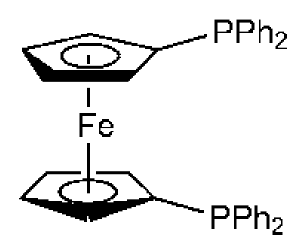
1. Friedel-Crafts reactions



2. Lithiation



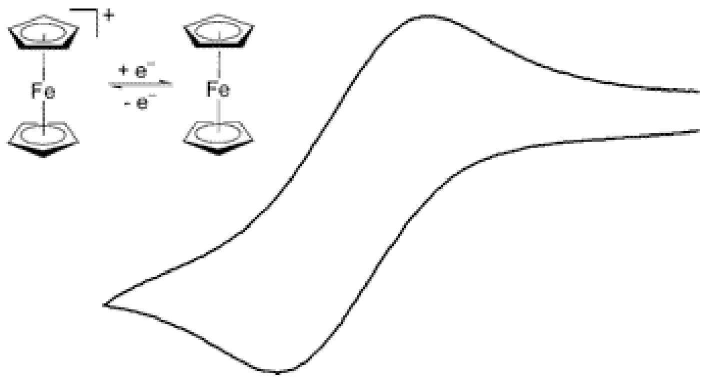


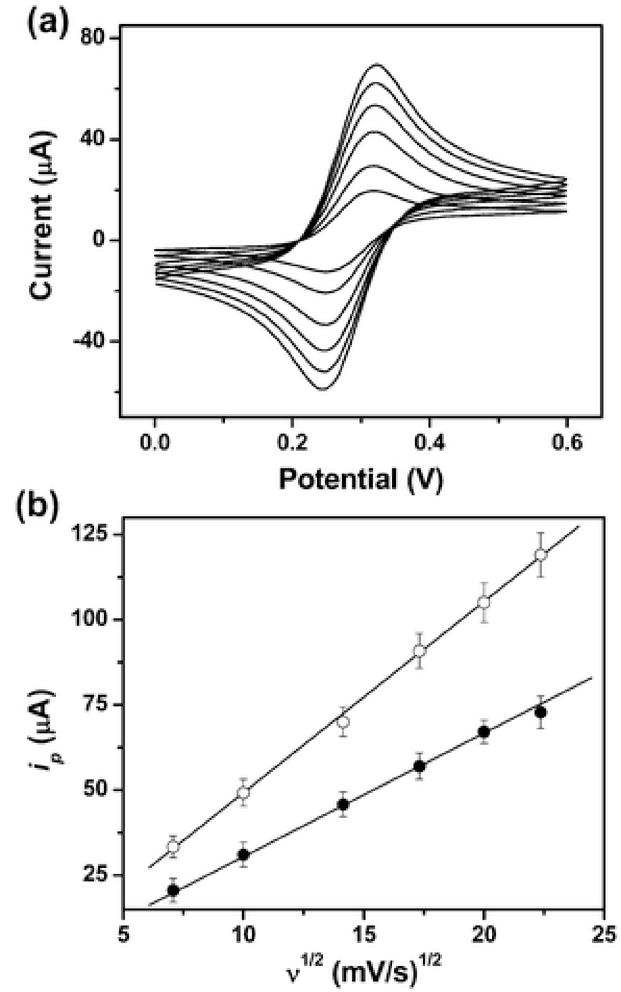


Good Nucleophile

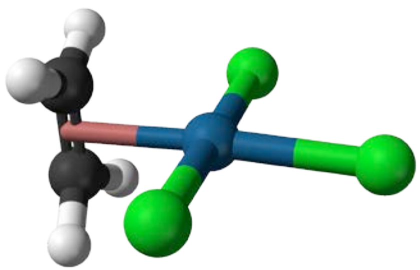
Applications of ferrocene

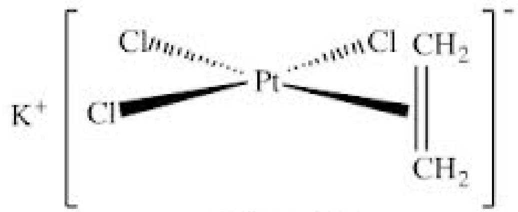
Solution Electrochemistry Standard



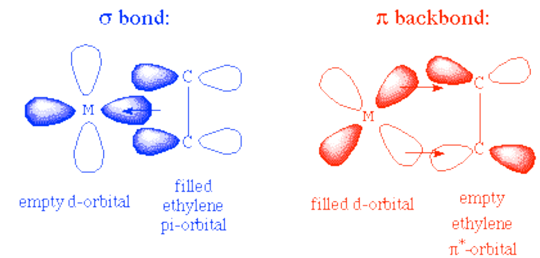


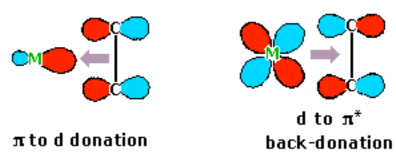
The first olefin complex: Zeise's salt. (1820's !)

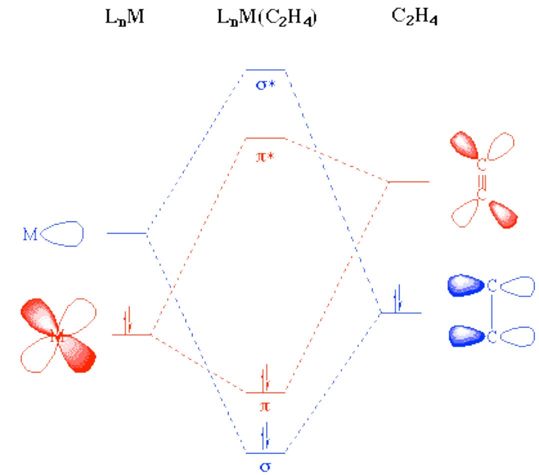


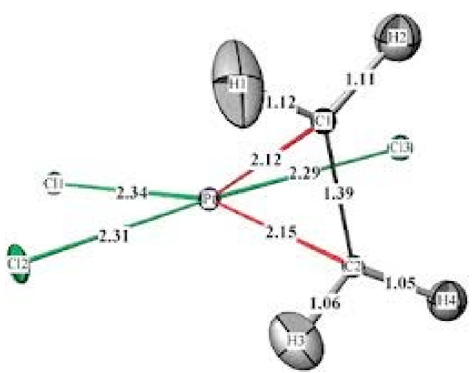


Zeise's Salt
Potassium trichloro(ethylene)platinate(II)









Properties of Werner-type Transition Metal Complexes

1. Highly colored (absorb light in visible, transmit light which eye detects)

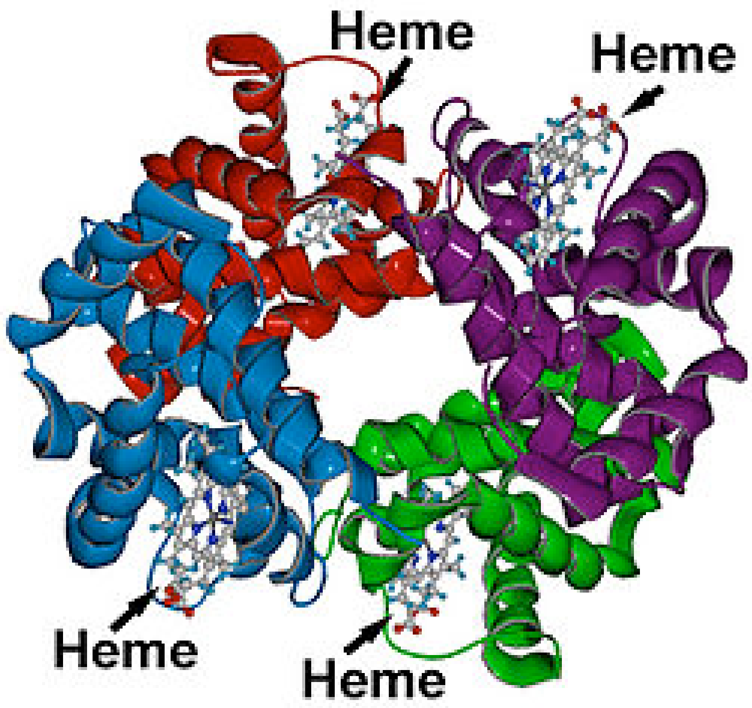
2. May exhibit multiple oxidation states

3. May exhibit paramagnetism as dependent on metal oxidation state and on ligand field.

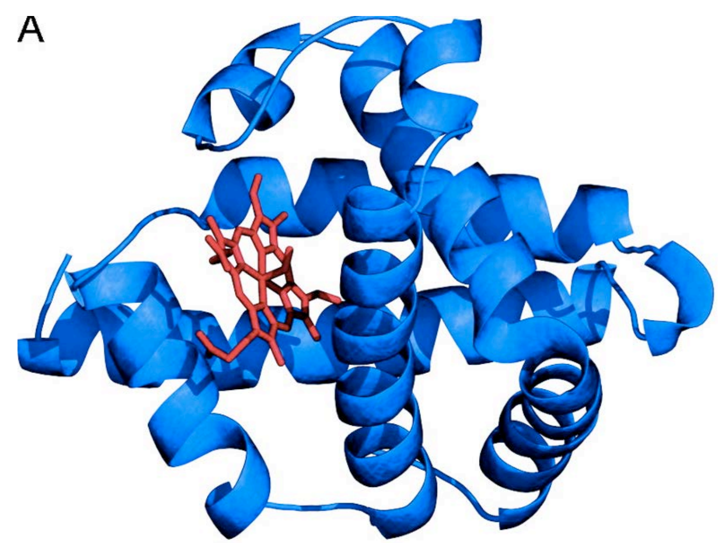
4. Reactivity includes:
   - **A) Ligand exchange processes:**
     - i) Associative (S_N2; expanded coordination no.)
     - ii) Dissociative (S_N1; slow step is ligand loss)
   - **B) Redox Processes**
     - i) inner sphere atom transfer;
     - ii) outer sphere electron processes)
     - iii) Oxidative Addition and Reductive Elimination

The magical porphyrin ligand: Hemoglobin, myoglobin and Other proteins have "Heme iron"
When oxygenated, hemoglobin is red and diamagnetic.
When deoxygenated, blue and paramagnetic!
What's going on here????

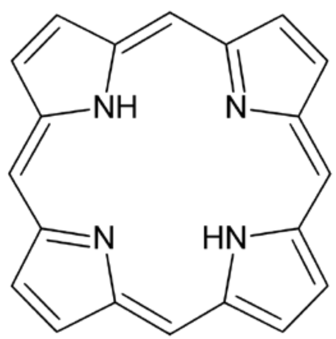
Hemoglobin (blood)



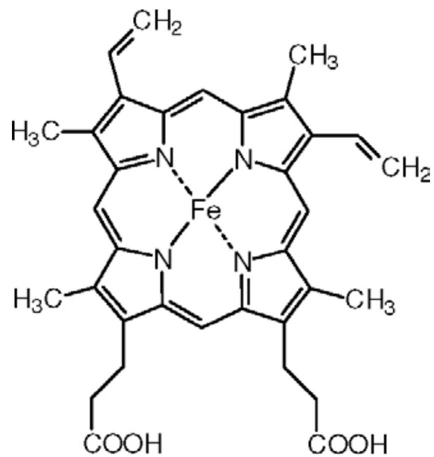
Myoglobin (muscles)



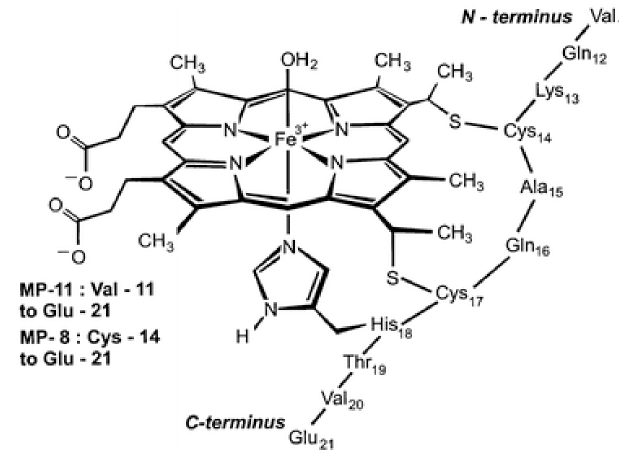
The magical porphyrin ligand



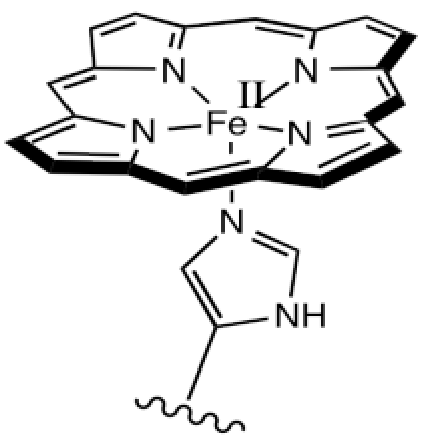
Protonated porphyrin ligand

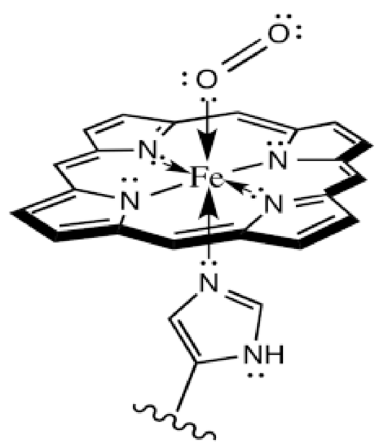


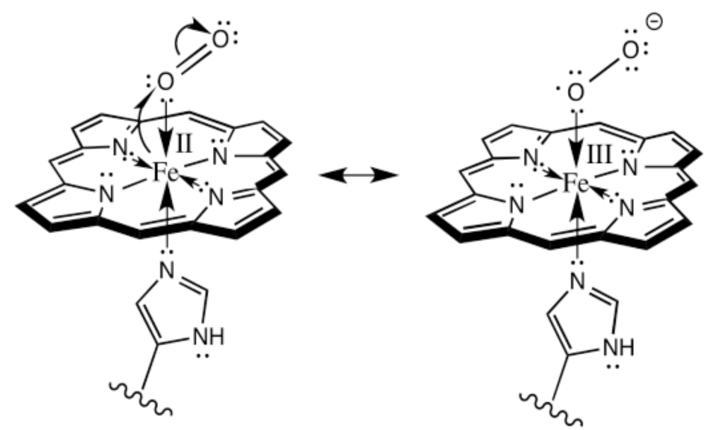
Heme Fe^{II}



Met-hemoglobin Fe^{III}







What's going on here? Inner or outer sphere redox process?

Overview of Transition Metal Complexes

1. The coordinate covalent or dative bond applies in L:→M

2. Lewis bases are called LIGANDS—all serve as σ-donors
   some are π-donors as well, and some are π-acceptors

3. Specific coordination number and geometries
   depend on metal and number of d-electrons

4. HSAB theory useful

   a) Hard bases stabilize high oxidation states

   b) Soft bases stabilize low oxidation states

Oxidation States in Transition Metals

element	ox. state range* (molecular compounds)	common (stable) ox. states**
Ti	0 → 4+	**3+**, **4+**
V	1- → 5+	**3+**, **4+**, **5+**
Cr	2- → 6+	**2+**, **3+**, **6+**
Mn	1- → 7+	**2+**, **3+**, 4+, **7+**
Fe	2- → 6+	0, **2+**, **3+**
Co	1- → 3+	**2+**, **3+**
Ni	0 → 4+	1+, **2+**, 3+
Cu	1+ → 3+	**1+**, **2+**
Zn	2+	**2+**

*Relative oxidation state stabilities are highly ligand-dependent; very rare oxidation states are omitted. **Most frequently encountered oxidation states in boldface.

Oxidation states and electronic configuration give a clue as to which ligands will form the more stable complexes and also to the coordination number (the number of ligands around the metal) of the metal within the complex.

4. Electron Configurations of Atoms and Common Oxidation States of the First Transition Series

Free Atom	Oxidation States				Atom in Molecule
$Sc(4s^2\ 3d^1)$	- -	$Sc^{3+}(d^0)$	- -	- -	- -
$Ti(4s^2\ 3d^2)$	- -	$Ti^{4+}(d^0)$	$Ti^{3+}(d^1)$	$Ti^{2+}\ (d^2)$	$Ti^0\ (d^4)$
$V(4s^2\ 3d^3)$	$V^{5+}\ (d^0)$	$V^{4+}(d^1)$	$V^{3+}(d^2)$	$V^{2+}\ (d^3)$	$V^0\ (d^5)$
$Cr(4s^1\ 3d^5)$	$Cr^{6+}\ (d^0)$	$Cr^{3+}(d^3)$	$Cr^{2+}(d^4)$	- -	$Cr^0\ (d^6)$
$Mn(4s^2\ 3d^5)$	$Mn^{7+}\ (d^0)$	$Mn^{3+}(d^4)$	$Mn^{2+}(d^5)$	- -	$Mn^0\ (d^7)$
$Fe(4s^2\ 3d^6)$	$Fe^{4+}\ (d^4)$	$Fe^{3+}(d^5)$	$Fe^{2+}(d^6)$	- -	$Fe^0\ (d^8)$
$Co(4s^2\ 3d^7)$	- -	$Co^{3+}(d^6)$	$Co^{2+}(d^7)$	$Co^{1+}\ (d^8)$	$Co^0\ (d^9)$
$Ni(4s^2 3d^8)$	- -	$Ni^{3+}(d^7)$	$Ni^{2+}(d^8)$	$Ni^{1+}\ (d^9)$	$Ni^0\ (d^{10})$
$Cu(4s^1\ 3d^{10})$	- -	$Cu^{3+}\ (d^8)$	$Cu^{2+}(d^9)$	$Cu^{1+}(d^{10})$	- -
$Zn(4s^2\ 3d^{10})$	- -	$Zn^{2+}(d^{10})$	- -	- -	- -

5. Oxidation State

Here, z = charge on the complex unit.

$$\boxed{\text{ox. state} = z - \sum_{N} \text{L charge}}$$

ligand removed from complex with closed shell configuration

examples:

positive oxidation states usually written as Roman numerals

octahedral: $[Co(CN)_6]^{3-} \rightarrow Co^{III} + 6CN^-$

Square pyramidal: $[MoOCl_4]^{1-} \rightarrow Mo^{V} + O^{2-} + 4Cl^-$

$[Rh(en)_2(NO_2)Cl]^{1+} \rightarrow Rh^{III} + 2en + NO_2^- + Cl^-$

Trigonal bi-pyramidal: $Fe(PF_3)_5 \rightarrow Fe^{0} + 5PF_3$

$[V(CO)_6]^{1-} \rightarrow V^{-I} + 6CO$

Tetrahedral: $[Fe_2S_2(SR)_4]^{3-} \rightarrow Fe^{II} + Fe^{III} + 2S^{2-} + 4RS^-$

$W(CH_3)_6 \rightarrow W^{VI} + 6CH_3^-$

> An oxidation state is a formalism which affords that d^n configuration consistent with molecular properties.

What geometries are prominent?

Octahedral

Trigonal Bipyramidal

Square planar

Tetrahedral

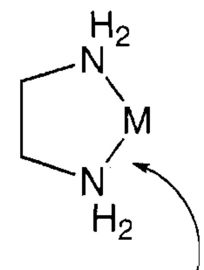
Trigonal planar

Linear

Classification of Ligands, I: type of donor orbitals involved: σ; σ + π; σ + π*; π+ π*

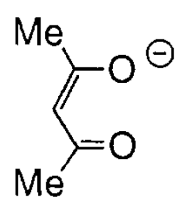
3. Ligands

- σ: NH_3, NR_3, $H_2N\sim\!\sim NH_2$ (en), $-CH_3$, $-C_2H_5$, ...
  σ-bonding only

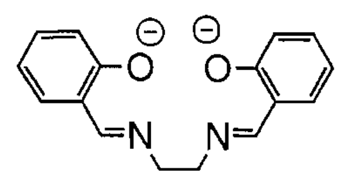


chelate ring

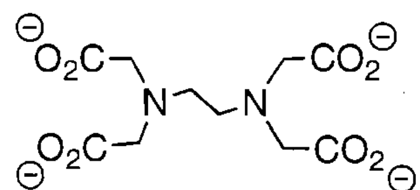
- σ + π (lp): π-donors
  F^-, Cl^-, Br^-, I^-, NCO^-, NCS^-, N_3^-, ...
  OH^-, OR^-, H_2O, O^{2-}
  R_2S, R_2Se, R_2Te
  SH^-, SR^-, S^{2-}, Se^{2-}, Te^{2-}
  R_2N^-, RN^{2-}, N^{3-}, R_2P^-, RP^{2-}, P^{3-}



acac
bidentate chelate



salen
tetradentate chelate

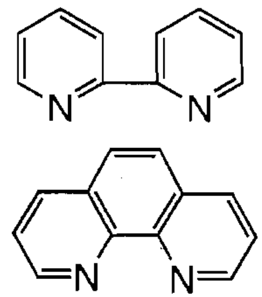


EDTA
hexadentate chelate

Ligands, Classification I, continued

- $\sigma + \pi^*/\sigma^*$ (vacant)
  back-acceptors
  π-acceptors
  π-acids

CO, CN^-, NO, N_2, RNC, R_3P, $(RO)_3P$, R_3As



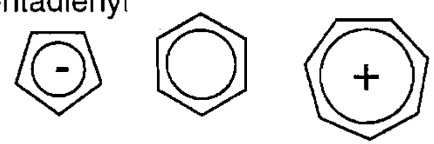
bpy

phen

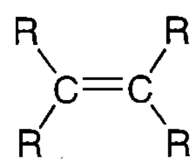
bidentate chelate

- $\pi + \pi^*$ (vacant)
  π-donors and
  π-acceptors

cyclopentadienyl



tropylium



R—C≡C—R

These ligands form *organometallic* molecules.

Classification of Ligands: II
The L, X, Z approach

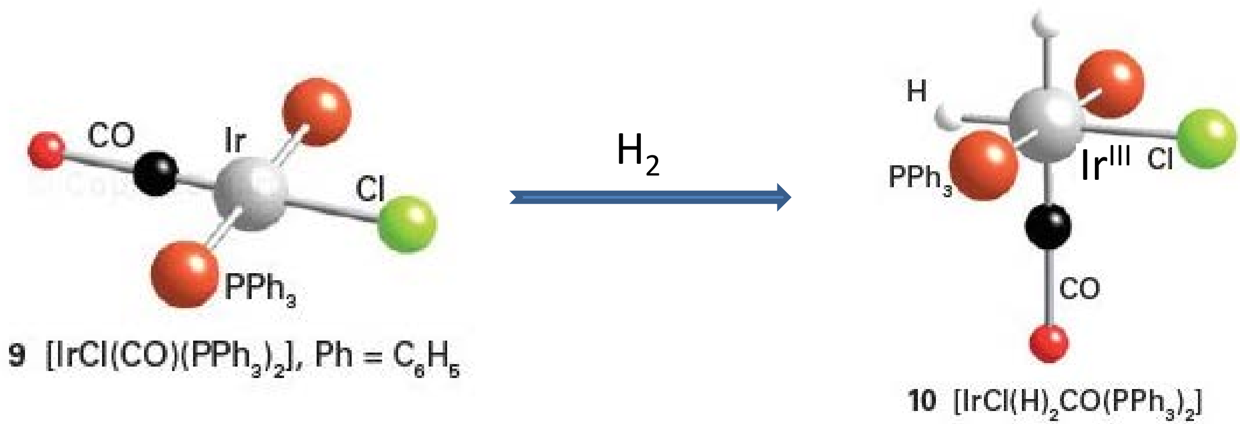
Malcolm Green : The CBC Method for Covalent Bond Classification used extensively in organometallic chemistry.

L ligands are derived from charge-neutral precursors: NH_3, amines, N-heterocycles such as pyridine, PR_3, CO, alkenes etc.

X ligands are derived from anionic precursors: halides, hydroxide, alkoxide alkyls—species that are one-electron neutral ligands, but two electron donors as anionic ligands. EDTA^{4-} is classified as an L_2X_4 ligand, features four anions and two neutral donor sites. C_5H_5 is classified an L_2X ligand.

Z ligands are RARE. They accept two electrons **from** the metal center. They donate none. The "ligand" is a Lewis Acid that accepts electrons rather than the Lewis Bases of the X and L ligands that donate electrons.

Oxidative addition of H_2 to chloro carbonyl bis triphenylphosphine Iridium(I) yields Chloro-dihydrido-carbonyl bis-triphenylphosphine Iridium(III). Note the neutral pre-Cursor, H_2, becomes two X^- ligands once added to Ir.



An ML_3X complex

An ML_3X_3 complex

Electron count: 16 e

18e

Ir(I) d^8 = 8 e

Ir(III) d^6 = 6 e

L ligands: 2 x (2) + 2 = 6

X- ligand: 2

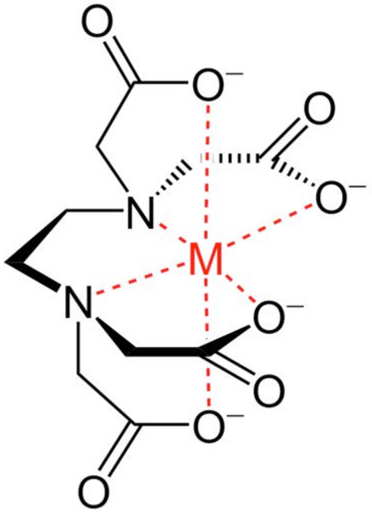
–

3 L ligands: 3 x 2 = 6

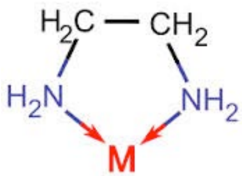
3 X^- ligands: 3 x 2 = 6

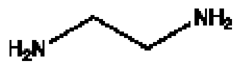
Classification of Ligands: III
A description of properties

- ❑ Strong Field/Weak Field Ligands
- ❑ Chelating Ligands and Denticity
  - ❖ Polydentate: bi-, tri-, tetra, penta-
  - ❖ Hexadentate, etc.
- ❑ Bridging Ligands
  - ❖ 4-electron bridge; 3 center, 4 electrons
  - ❖ 2-electron bridge; 3-center, 2 electrons
- ❑ Ambidentate Ligands
- ❑ Bulky Ligands
- ❑ Chiral Ligands
- ❑ Hemi-labile Ligands
- ❑ Non-innocent Ligands
- ❑ Spectator Ligands



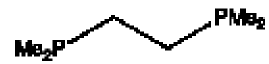
Chelating Ligands/Polydentate Ligands--examples



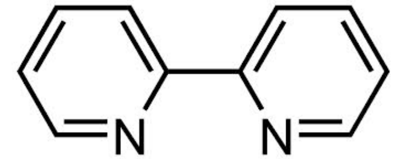


ethylenediamine (en)

b)

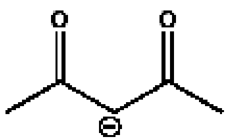


dimethylphosphinoethane (dmpe)



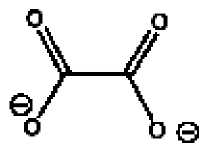
4,4'-bipyridine

c)

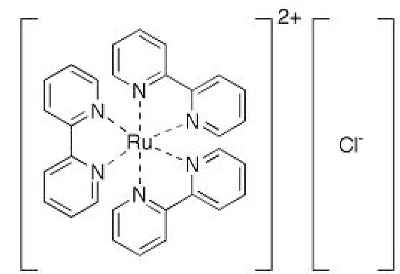


acetylacetonate (acac)

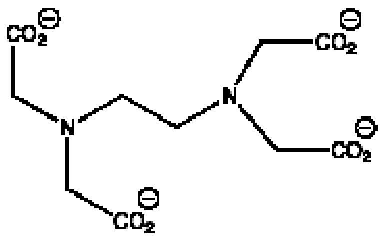
d)



oxalate (ox)

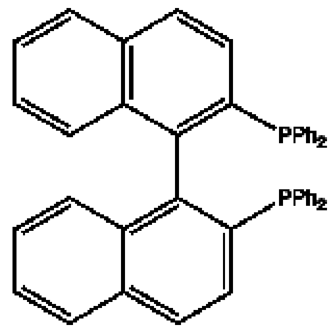


e)

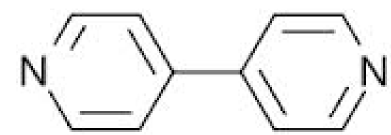


ethylenediamine tetraacetate (edta)

f)

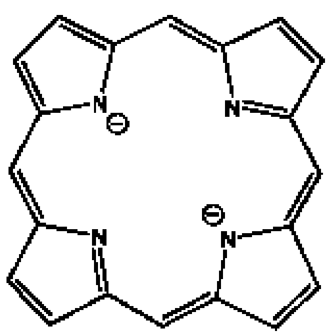


BINAP



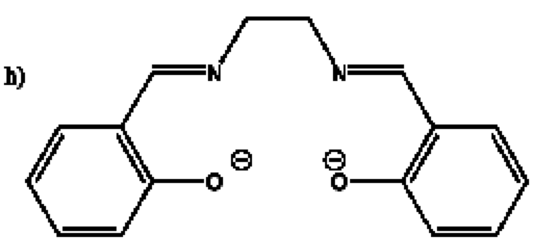
4,4'-bipyridine

g)



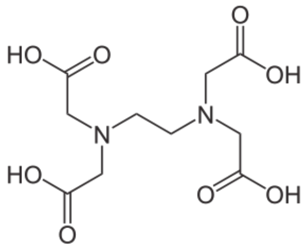
porphine (from porphyrin family)

h)

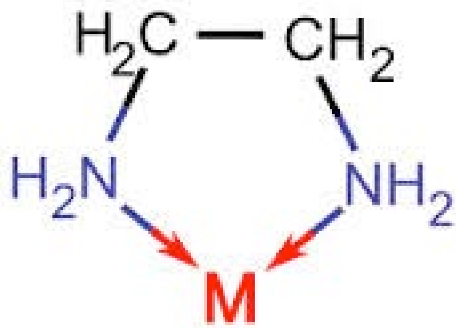


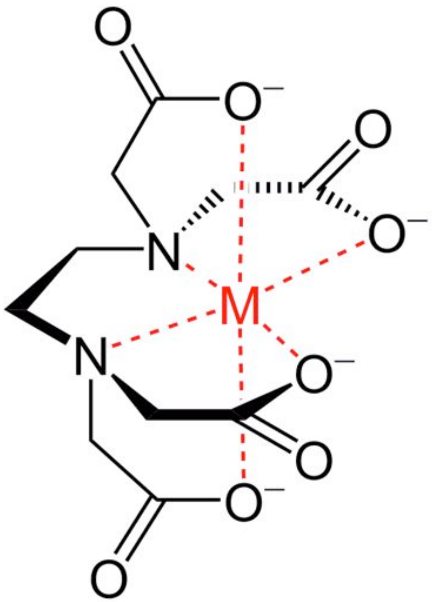
salen

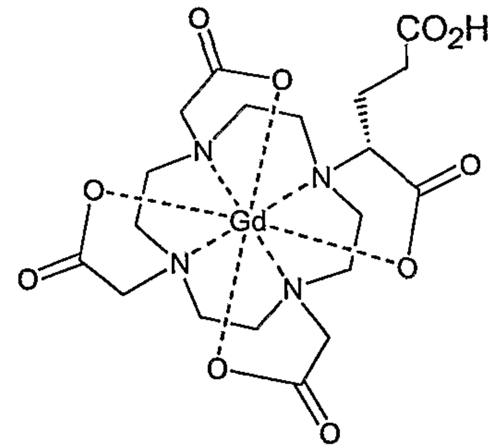
Chelating Ligands/Polydentate Ligands



Ethylenediamine:
An L_2 bidentate ligand

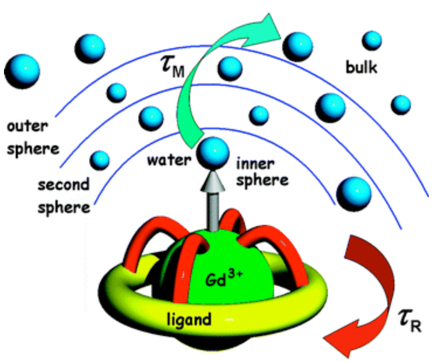






Ethylenediaminetetraacetate:

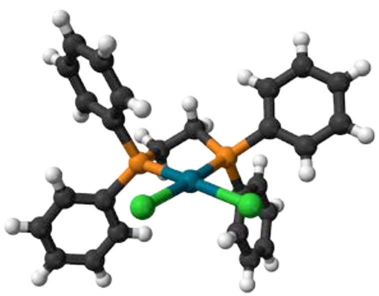
An L_2X_4, hexadentate ligand, an exceptional chelating agent with many uses. In medicine, for lead and mercury poisoning; also for thalassaemia (iron overload).

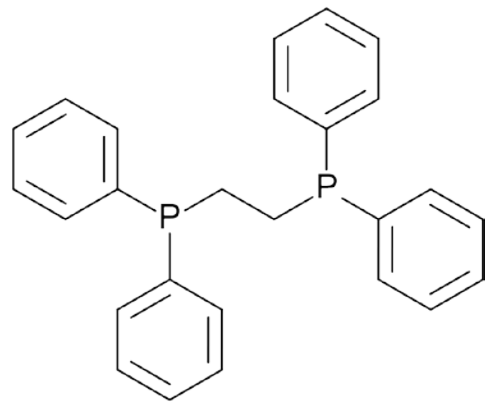


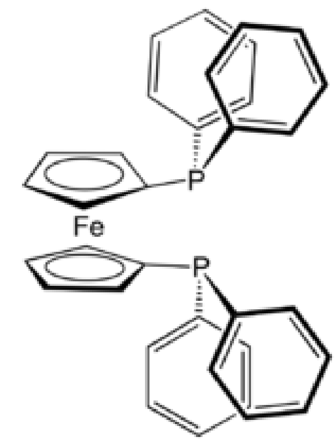
1,2-Bis(diphenylphosphino)ethane: $Ph_2PCH_2H_2PPh_2$

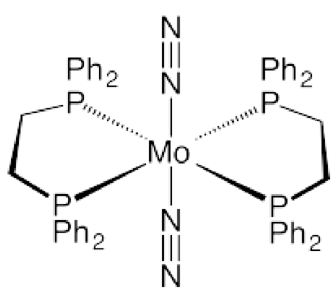
$$P(C_6H_5)_3 + 2\ Na^0 \rightarrow Na^+P(C_6H_5)_2^- + Na^+C_6H_5^-$$

$$2\ NaP(C_6H_5)_2 + ClCH_2CH_2Cl \rightarrow (C_6H_5)_2PCH_2CH_2P(C_6H_5)_2 + 2\ NaCl$$

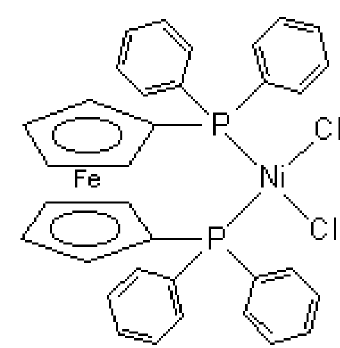








NOTE: Images for these In Google/internet search are TERRIBLE.



So, how do we mix and match these ligands and metals with their various oxidation states to get stable molecules?

1. Hard/Soft Acid Base Approach to stability

2. Knowledge of preferred coordination numbers and geometries

The Chemical Bond:

a) The sharing of an electron pair between two atoms.
b) A mixture of electrostatic and covalent interaction.

- high oxidation states stabilized by anionic π-donor ligands of electronegative atoms

- low oxidation states stabilized by neutral π-acceptor ligands

examples:

	"high"	"low"
Ti	$[TiF_6]^{2-}$, TiO_2	$Ti(Me_2PCH_2CH_2PMe_2)_2Cl_2$
V	$[VF_6]^{2-}$, $[VOCl_4]^{1-}$, $[VO_2Cl_2]^{1-}$	$[V(CO)_6]^{0,1-}$
Cr	$[CrO_4]^{2-}$, $[CrOCl_4]^{1-}$, $[CrF_6]^{2-}$	$[Cr(CNR)_6]^{1+}$, $Cr(CO)_6$, $[Cr(CO)_5]^{2-}$
Mn	$[MnO_4]^{1-,2-}$, $[MnCl_6]^{2-}$	$Mn(CO)_5Cl$, $Mn_2(CO)_{10}$, $[Mn(CO)_5]^{1-}$
Fe	$[FeO_4]^{2-}$, $[FeCl_4]^{1-}$	$Fe(CO)_5$, $Fe(PF_3)_5$, $[Fe(CO)_4]^{2-}$
Co	$[CoF_6]^{3-}$, $[Cr(en)_3]^{3+}$	$[Co(CO)_4]^{1-}$, $Co(CO)_3NO$, $Co_2(CO)_8$, $Co(PR_3)_3Br$
Ni	$[NiF_6]^{2-}$, $[Ni(diars)_2Cl_2]^{1+}$	$Ni(CO)_4$, $Ni(PF_3)_4$, $Ni(PR_3)_3Br$, $[Ni_2(CN)_6]^{4-}$
Cu	$[CuF_6]^{3-}$	$[Cu(CN)_2]^{1-}$, $[CuCl_2]^{1-}$

At parity of ligand and coordination number, higher oxidation states become increasingly stable down a vertical group.

But, is the oxidation state the actual charge on the metal?? Let's Ask Linus Pauling. . .

6. Electroneutrality Principle:

In any molecule, bonding electrons are distributed in such a way that individual atoms are as close to electroneutrality as possible.

$$L\!:^{z-} + M^{z+} \rightarrow \overset{\delta-}{L}\!-\!M^{\delta+}$$

Metal-ligand bond formation tends to reduce +ve charge on M (and -ve charge on L^{z-}), with the result that the *actual* charge on M is much below that corresponding to its oxidation state. The oxidation state conveys the d^n configuration of the coordinated metal.

Table 3.1 Anions and their names when acting as ligands

Free anion	Coordinated anion
Amide (NH_2^-)	amido (or azanido)
Azide (N_3^-)	nitrido (azido will also be met)
Bromide (Br^-)	bromo
Carbonate (CO_3^{2-})	carbonato
Cyanate (CNO^-)	cyanato
Fluoride (F^-)	fluoro (*not* fluo)
Hydroxide (OH^-)	hydroxo (or hydroxido or hydroxy)
Nitrite (NO_2^-)	nitro or nitrito-N (see text)
Oxide (O^{2-})	oxo (or oxido)
Thiocyanate $(SCN)^-$	thiocyanato-N (N-bonded), thiocyanato-S (S-bonded)

Table 7.1 Typical ligands and their names

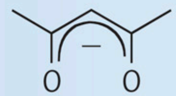
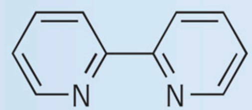
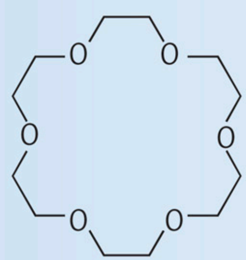
Name	Formula	Abbreviation	Donor atoms	Number of donors
Acetylacetonato		$acac^-$	O	2
Ammine	NH_3		N	1
Aqua	H_2O		O	1
2,2-Bipyridine		bpy	N	2
Bromido	Br^-		Br	1
Carbanato	CO_3^{2-}		O	1 or 2
Carbonyl	CO		C	1
Chlorido	Cl^-		Cl	1
1,4,7,10,13,16-Hexaoxa-cyclooctadecane		18-crown-6	O	6

Table 7.1 *(Continued)*

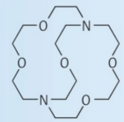
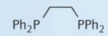
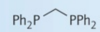
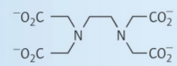
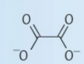
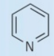
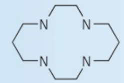
Name	Formula	Abbreviation	Donor atoms	Number of donors
4,7,13,16,21-Pentaoxa-1, 10-diaza-bicyclo [8.8.5]tricosane		2.2.1 crypt	N, O	2N, 5O
Cyanido	CN^-		C	1
Diethylenetriamine	$NH(CH_2CH_2NH_2)_2$	dien	N	3
Bis(diphenylphosphino)ethane		dppe	P	2
Bis(diphenylphosphino)methane		dppm	P	2
Cyclopentadienyl	$C_5H_5^-$	Cp^-	C	5
Ethylenediamine (1,2-diaminoethane)	$NH_2CH_2CH_2NH_2$	en	N	2
Ethylenediaminetetraacetato		$edta^{4-}$	N, O	2N, 4O
Fluorido	F^-		F	1
Glycinato	$NH_2CH_2CO_2^-$	gly	N, O	1N, 1O
Hydrido	H^-		H	1
Hydroxido	OH^-		O	1
Iodido	I^-		I	1
Nitrato	NO_3^-		O	1 or 2
Nitrito−κ*O*	NO_2^-		O	1
Nitrito−κ*N*	NO_2^-		N	1
Oxido	O^{2-}		O	1
Oxalato		ox	O	2
Pyridine		py	N	1
Sulfido	S^{2-}		S	1
Tetraazacyclotetradecane		cyclam	N	4
Thiocyanato−κ*N*	NCS^-		N	1
Thiocyanato−κ*S*	SCN^-		S	1
Thiolato	RS^-		S	1
Triaminotriethylamine	$N(CH_2CH_2NH_2)_3$	tren	N	4
Tricyclohexylphosphine	$P(C_6H_{11})_3$	PCy_3	P	1
Trimethylphosphine	$P(CH_3)_3$	PMe_3	P	1
Triphenylphosphine	$P(C_6H_5)_3$	PPh_3	P	1

Table 7.2 Prefixes used for naming complexes

Prefix	Meaning
mono-	1
di-, bis-	2
tri-,tris-	3
tetra-, tetrakis-	4
penta-	5
hexa-	6
hepta-	7
octa-	8
nona-	9
deca-	10
undeca-	11
dodeca-	12

Naming transition metal complexes:

1) Cations first, anions second.
2) Within the coordination complex:
   - anion ligands first, neutral ligands second, metals last
   - give oxidation state of metal in parentheses
   - if anionic complex, add "ate" to metal name
   - if cationic complex, the metal, followed by ox. state, then the ligands

   and then counter anions. No need to give number of counter anions

Table 3.2 Examples of the nomenclature of simple coordination compounds. Some of these examples contain, and adequately define, points not explicitly covered in the text

Compound	Nomenclature
$K_2[ReF_8]$	potassium octafluororhenate (note: only 'potassium')
$[Cu(NH_3)_4]SO_4$	tetraamminecobalt(II) sulfate (note: 'aa' and 'mm')
$[CuCl_2(py)_2]$	dichlorobispyridinecopper(II) (note: bipyridine is the present name for the 2,2′-bipyridine ligand—see Table 2.3. More strictly, and as in the text, di(pyridine) should be used to give dichlorodi(pyridine)copper(II). However, in the spoken language an ambiguity can arise)
$[Hg(C_2H_5)_2]$	diethylmercury(II)
$[Ni(PPh_3)_4]$	tetra(triphenylphosphine)nickel(0)
$[Ru(NH_3)_5(N_2)]^{2+}$	pentaamminedinitrogenruthenium(II) (note: similarly, O_2 is dioxygen, but beware confusion with O_2^-, superoxo and O_2^{2-}, peroxo)
$K_2[FeCl_4]$	potassium tetrachloroferrate(II)
$(NH_4)_2[SnCl_6]$	ammonium hexachlorostannate(IV)

Isomerism

all isomers of a molecule

atom connectivity

same | different

stereoisomers

molecules with the same empirical formula and atom-to-atom bonding sequence (connectivity) but differing atomic spatial arrangements

constitutional isomers

ionization, solvate, coordination, linkage

enantiomers

non-superimposable mirror images

lack S_n axis (no i or σ)

chiral

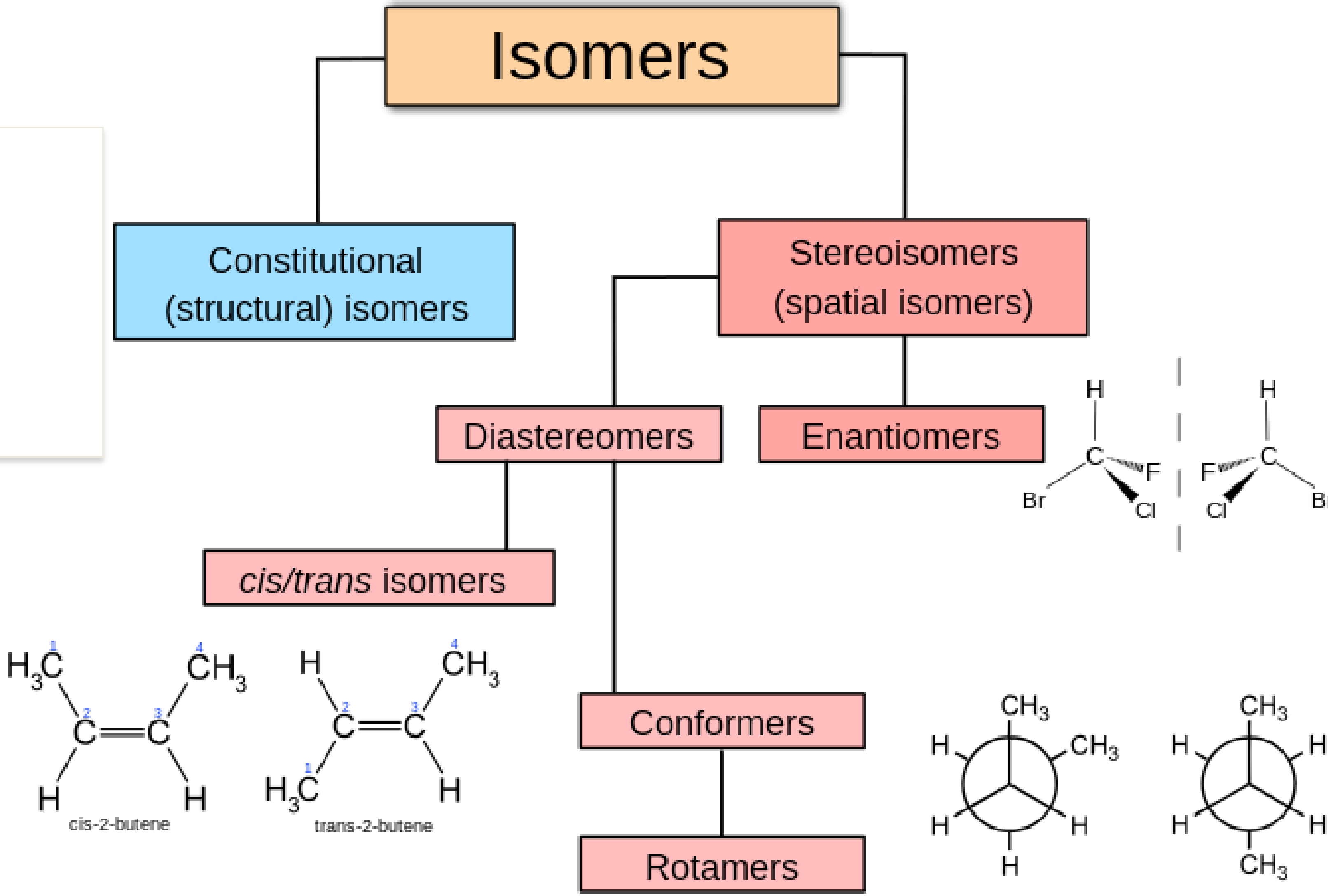
diastereomers

stereoisomers that are not enantiomers

achiral

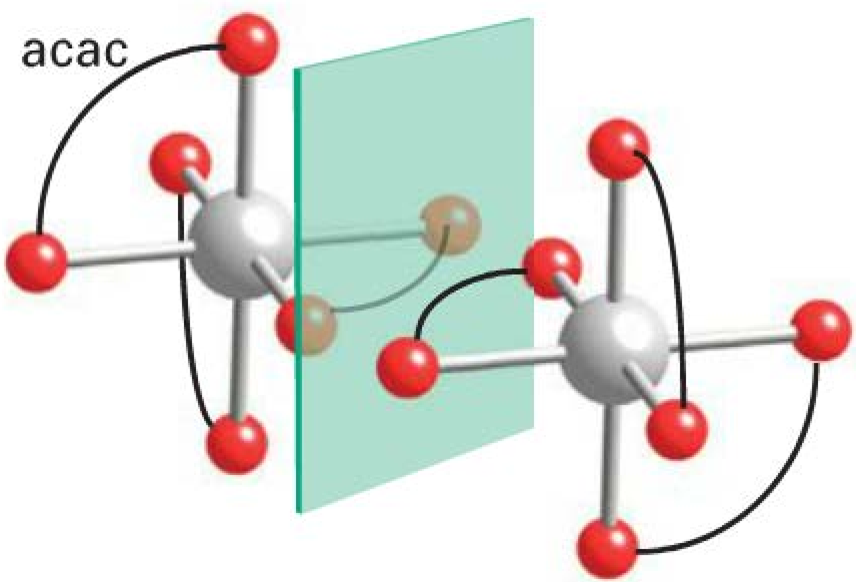
Examples:

$[Cr(OH_2)_5NCS]^{2+}$ $[Cr(OH_2)_5SCN]^{2+}$ *linkage isomers*

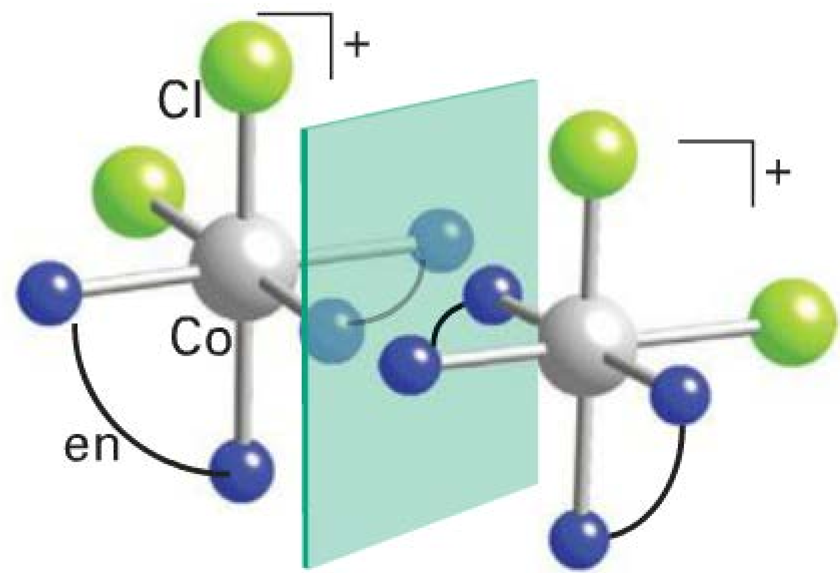


Isomers
Constitutional (structural) isomers
Stereoisomers (spatial isomers)
Diastereomers
Enantiomers
cis/trans isomers
Conformers
Rotamers
cis-2-butene
trans-2-butene

Structural isomers: diastereomers

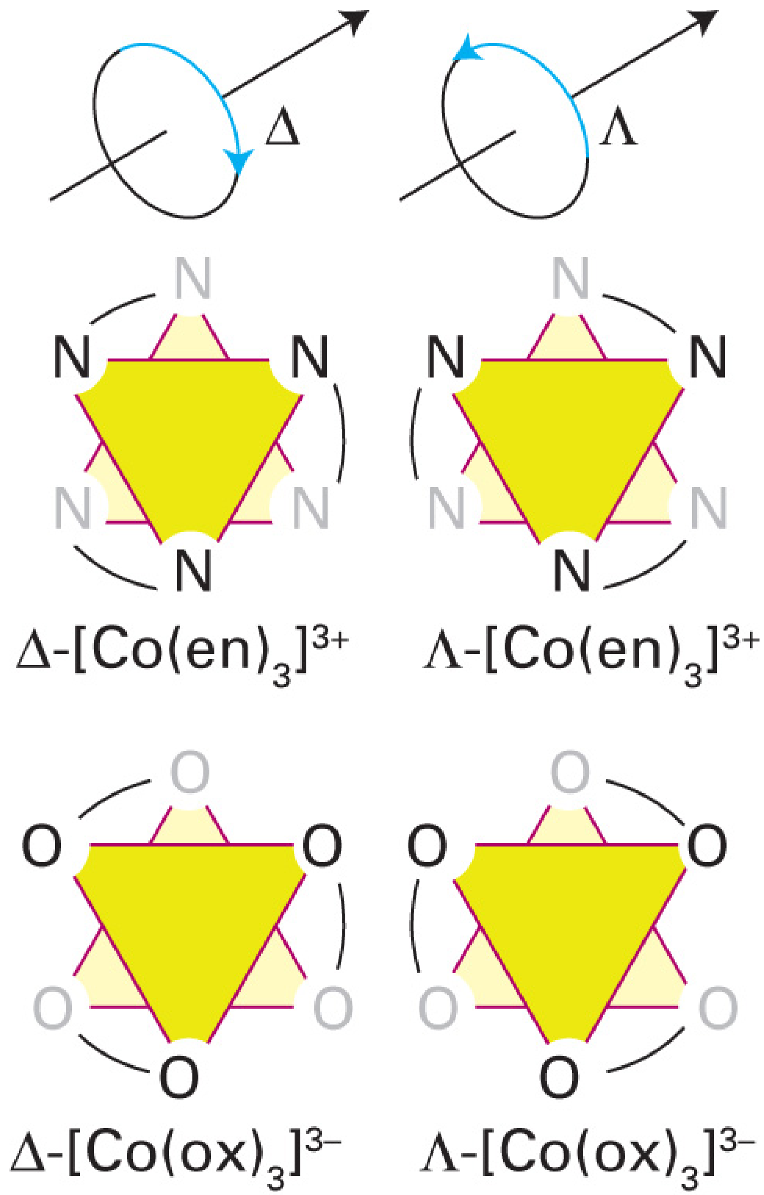


66 [Mn(acac)$_3$] enantiomers

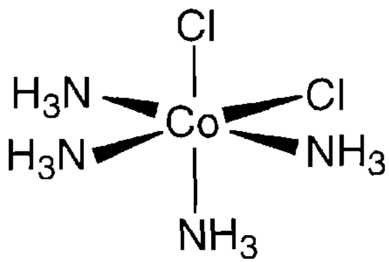


67 *cis*-[CoCl$_2$(en)$_2$]$^+$ enantiomers

2 diastereomers

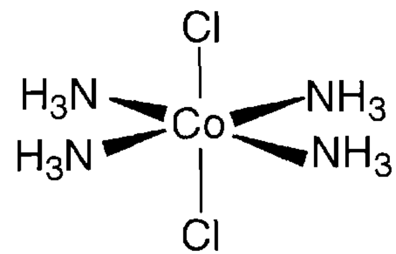

Δ
Λ
Δ-[Co(en)3]3+
Λ-[Co(en)3]3+
Δ-[Co(ox)3]3–
Λ-[Co(ox)3]3–

$[Co(NH_3)_4Cl_2]^+$



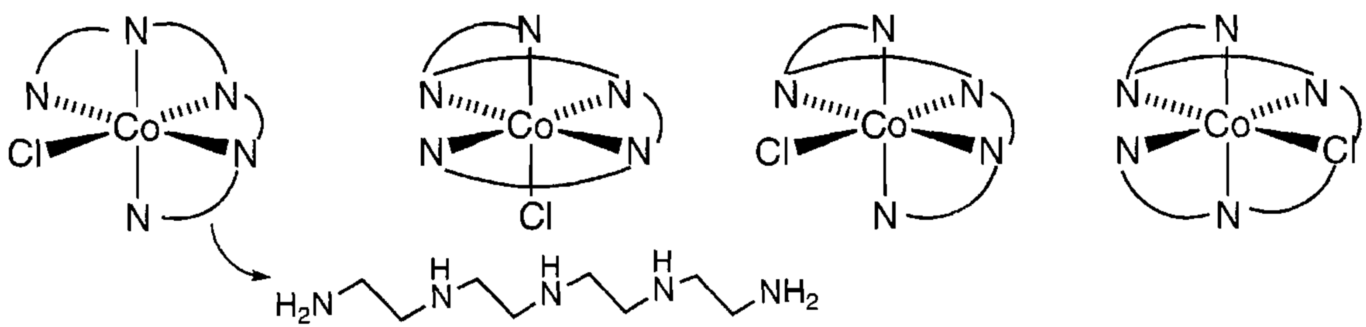
cis C_{2v}

2 diastereomers



trans D_{4h}

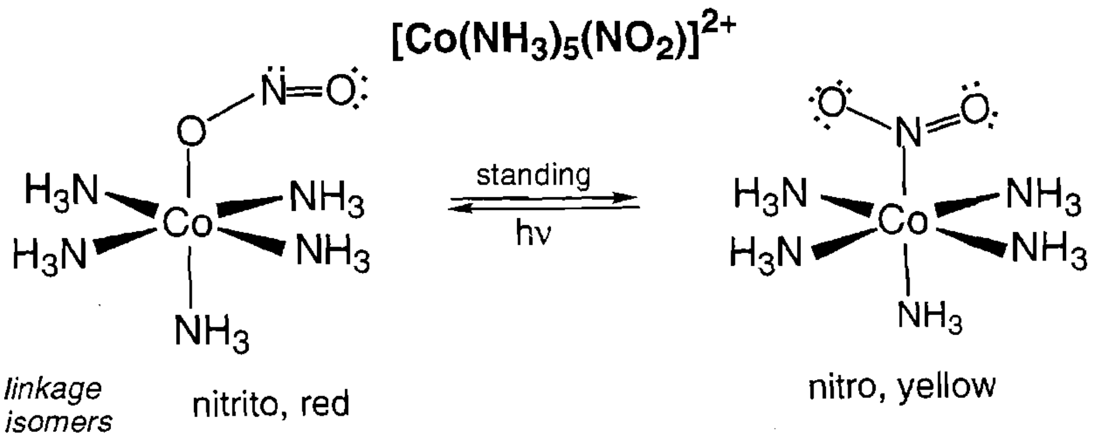
$[Co(tetren)Cl]^{2+}$



each isomer is chiral

Isomers because of the Ligand:

Linkage isomers or Ambi-dentate ligands



Isomers because of the Ligand:

Chirality within the ligand

So, How do we measure stability?

Formation Constant:

$$\Delta G^0 = -RT\ln K_{eq}$$

$$\Delta G^0 = \Delta H^0 - T\Delta S$$

● Irving-Williams Stability Order

For the reactions $M + nL \rightleftharpoons ML_N$, the following order of stability constants holds under the indicated conditions (very few exceptions).

$$K_M: \boxed{Mn < Fe < Co < Ni < Cu > Zn}$$

conditions: M has same charge and is high-spin

does not include Cu(II) binding of axial ligands

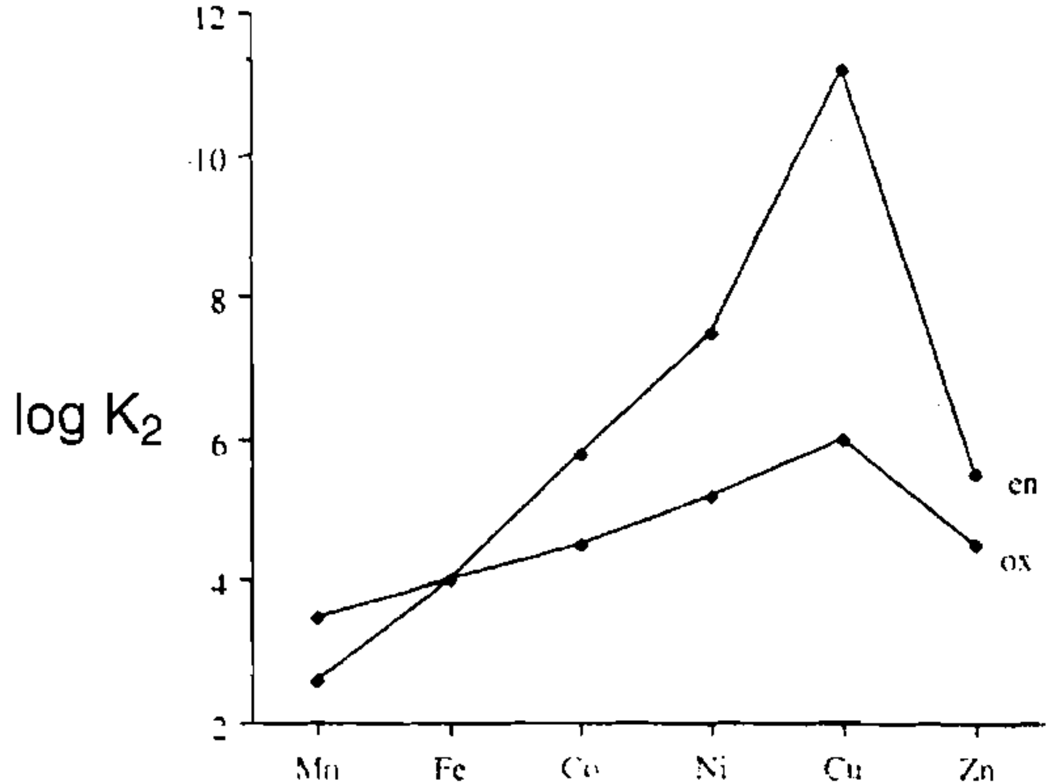
$$[M(OH_2)_6]^{2+} + H_2N\frown NH_2 \rightleftharpoons [M(en)(OH_2)_4]^{2+} + 2H_2O \qquad K = 10^{+xx}$$

quantity	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$\log K_1$ (M^{-1})	2.79	4.33	5.94	7.70	10.7	5.78
$-\Delta G_{298}$ (kcal/mol)	3.80	5.90	8.10	10.5	14.6	7.89
$-\Delta H$ (kcal/mol)*	2.80	5.09	6.88	8.89	13.0	6.69
$T\Delta S_{298}$ (kcal/mol)	1.0	0.81	1.2	1.6	1.6	1.2

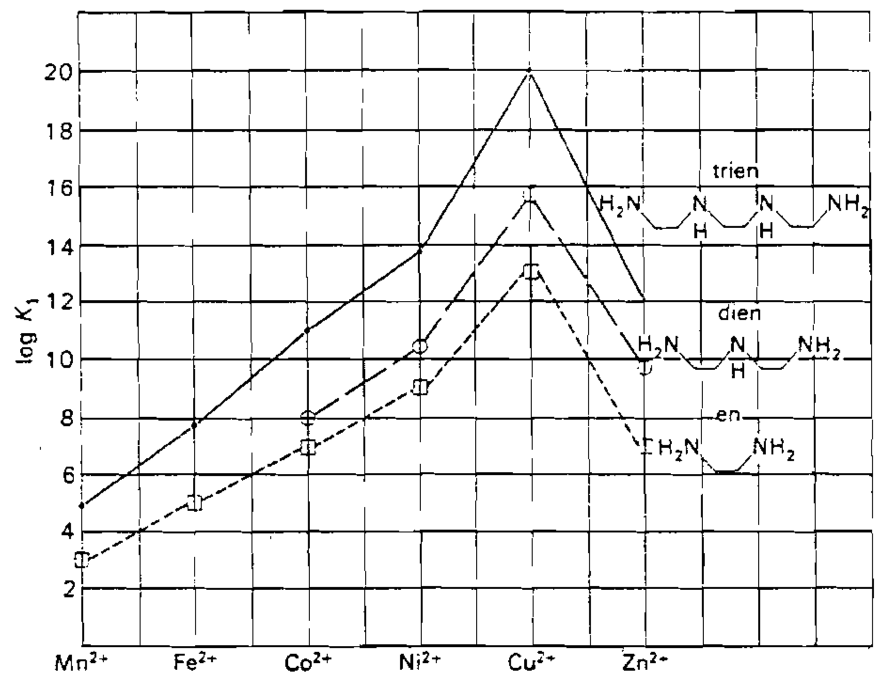
*determined calorimetrically

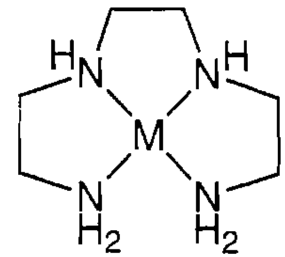
Reaction is favored enthalpically and entropically, but with
$|\Delta H| \gg T\Delta S$

Similar results for K_2 reaction.

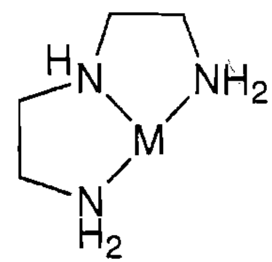


● number of chelate rings

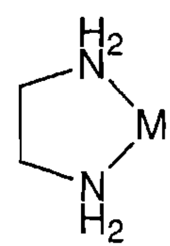




3 rings

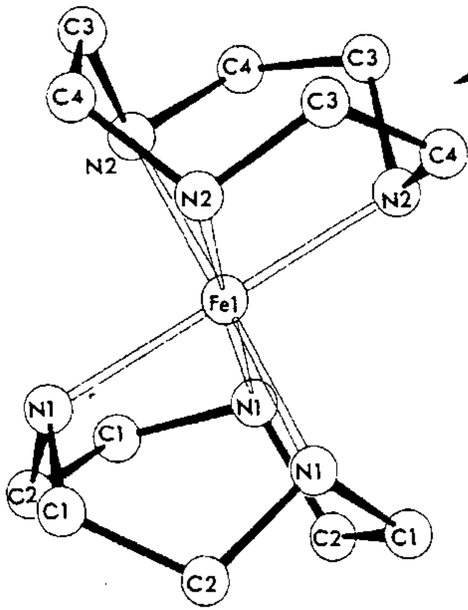


2 rings



1 ring

Stability increases because enthalpy becomes increasingly negative (increased number of M–N bonds) and entropy increases (more water molecues released).



$[Fe(tacn)_2]^{2+}$

1,4,7-triazacyclononane (tacn)
3 rings/ligand

tacn forms relatively stable complexes with $M^{2+,3+}$

$$[M(OH_2)_6]^{2+} + \text{tacn} \rightleftharpoons [M(\text{tacn})(OH_2)_3]^{2+} + 3H_2O$$

	$\log K_1$
Ni(II)	16.24
Cu(II)	17.5
Zn(II)	11.6

favorable ΔH, ΔS;
difficult to break M–N bonds because of semi-rigid ligand structure

The Chelate Effect

- **Chelate effect**

compare stability constants (298 K):

	log β, K
$[Ni(OH_2)_6]^{2+} + 2NH_3 \rightleftharpoons [Ni(NH_3)_2(OH_2)_4]^{2+} + 2H_2O$	5.04
$[Ni(OH_2)_6]^{2+} + en \rightleftharpoons [Ni(en)(OH_2)_4]^{2+} + 2H_2O$	7.45
$[Ni(NH_3)_2(OH_2)_4]^{2+} + 2NH_3 \rightleftharpoons [Ni(NH_3)_4(OH_2)_2]^{2+} + 2H_2O$	0.78
$[Ni(NH_3)_2(OH_2)_4]^{2+} + en \rightleftharpoons [Ni(en)_2(OH_2)_4]^{2+} + 2NH_3$	2.41
$[Ni(NH_3)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6NH_3$	9.67

$\Delta H = -2.89$ kcal/mol   small favorable contribution

$\Delta H_{SE} = -2.75$ kcal/mol

$T\Delta S = 13.2$ kcal/mol

entropy increase (4→7 particles) dominates reaction

(even though NH_3 more strongly solvated than en)

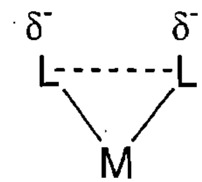
The Chelate Effect

$$[Cu(NH_3)_2(OH_2)_4]^{2+} + en \rightleftharpoons [Cu(NH_3)_2(en)(OH_2)_2]^{2+} + 2H_2O$$

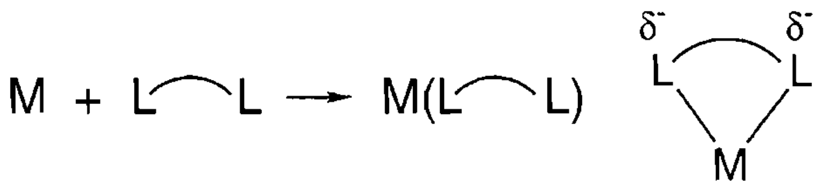
$\Delta G = -3.70$ kcal/mol $\quad \Delta H = -1.91$ kcal/mol $\quad T\Delta S = 1.79$ kcal/mol

favorable 2→3 particles)

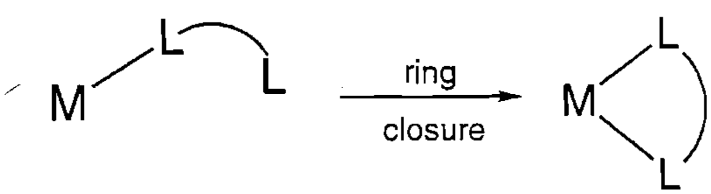
$$M + 2L \longrightarrow ML_2$$



repulsion



repulsion "built in"



Once the first M–L bond is formed, there is a high probability the second bond will form because of the proximity of the other L atom. Corresponding probability is much lower with two unidentate ligands.

Now, How about those colors and the magnetism?

Where are the electrons? Show me the electrons!!

Color: Electronic transitions due to energy levels whose gaps are in the visible range of the electromagnetic spectrum.

Magnetism: partially filled orbitals, unpaired electrons.

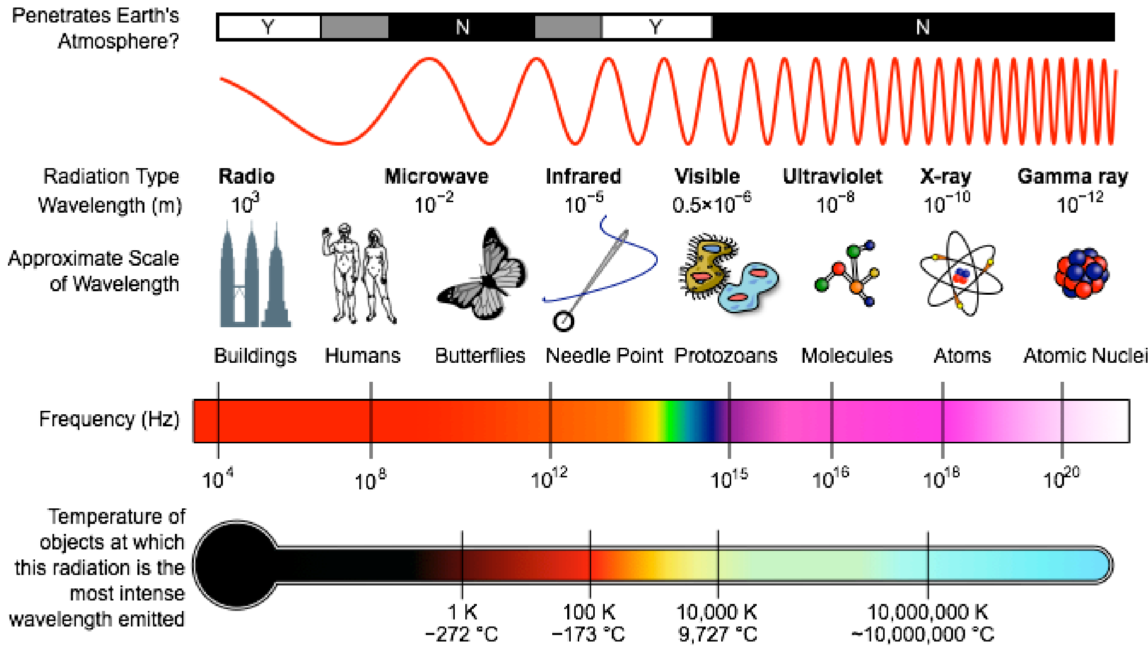
high spin: maximum no. of d electrons unpaired

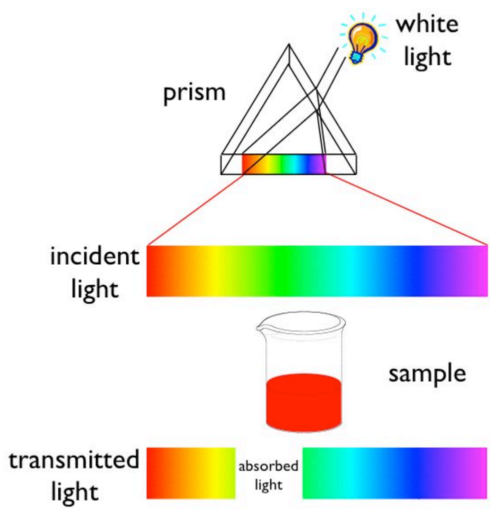
low spin: electrons paired up in d orbitals. WHY??

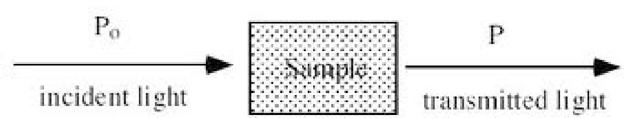
Bonding models: **Valence bond (coordinate covalent bond needs empty orbitals on metal)**

Molecular Orbital Theory (all orbitals defined)

Crystal Field Theory (originally from ionic crystals; influence of ligand lone pair repulsion on d-orbitals)

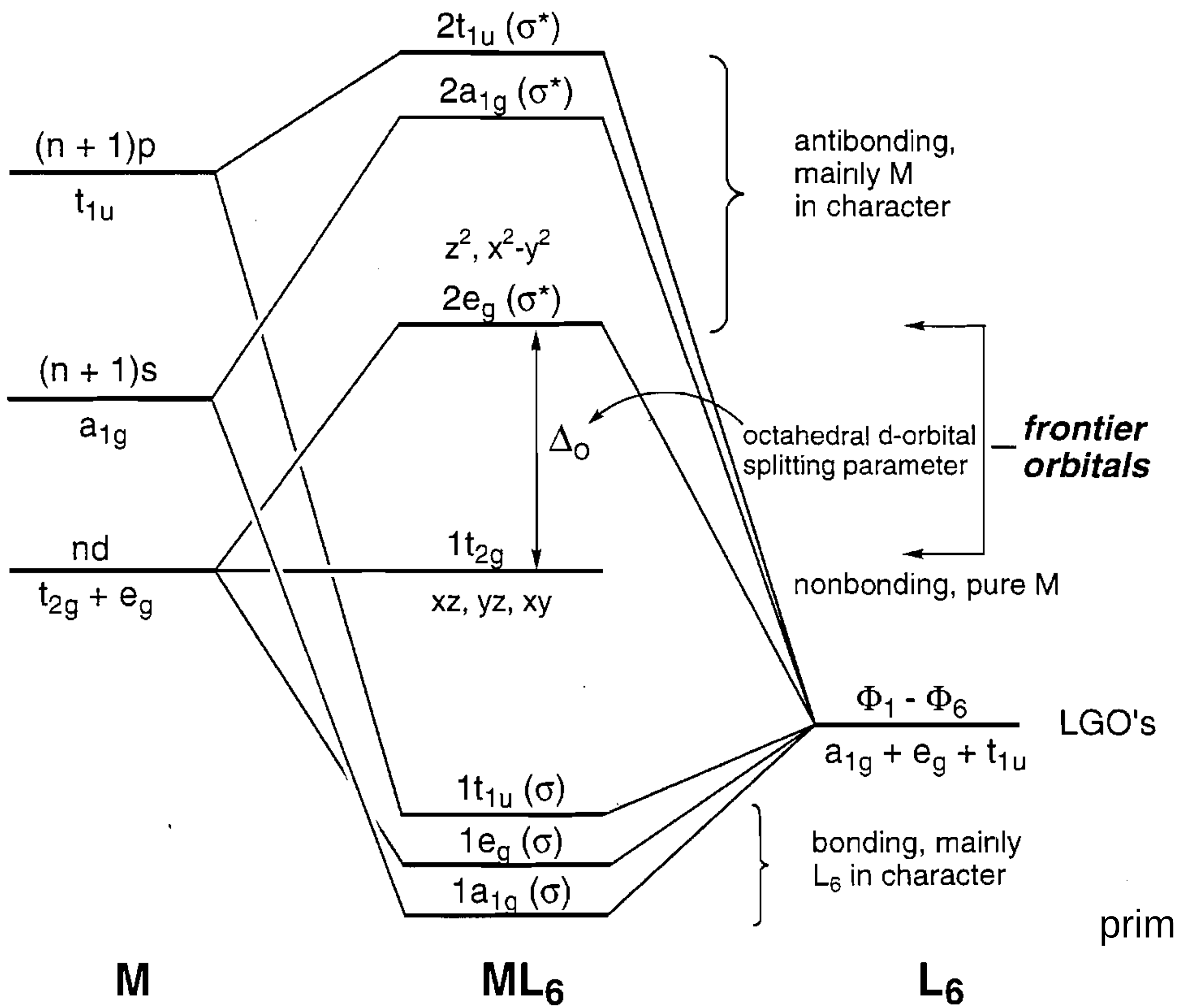






$$\text{Transmittance} = \frac{P}{P_0} = \frac{\text{intensity of transmitted light}}{\text{intensity of incident light}}$$

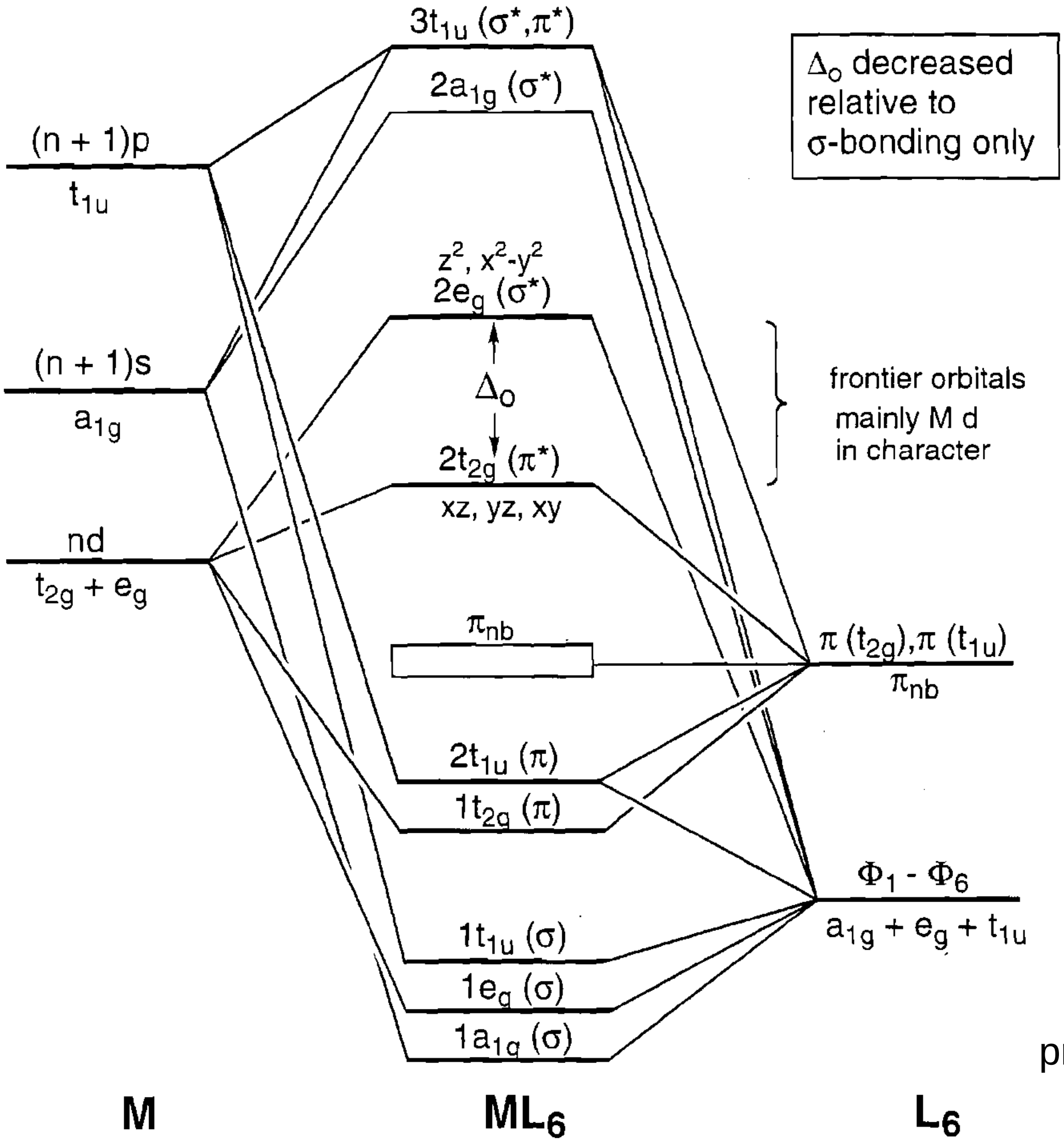
To explain magnetism and colors, need electronic configuration of the Transition Metal Complex



prime example

NH_3

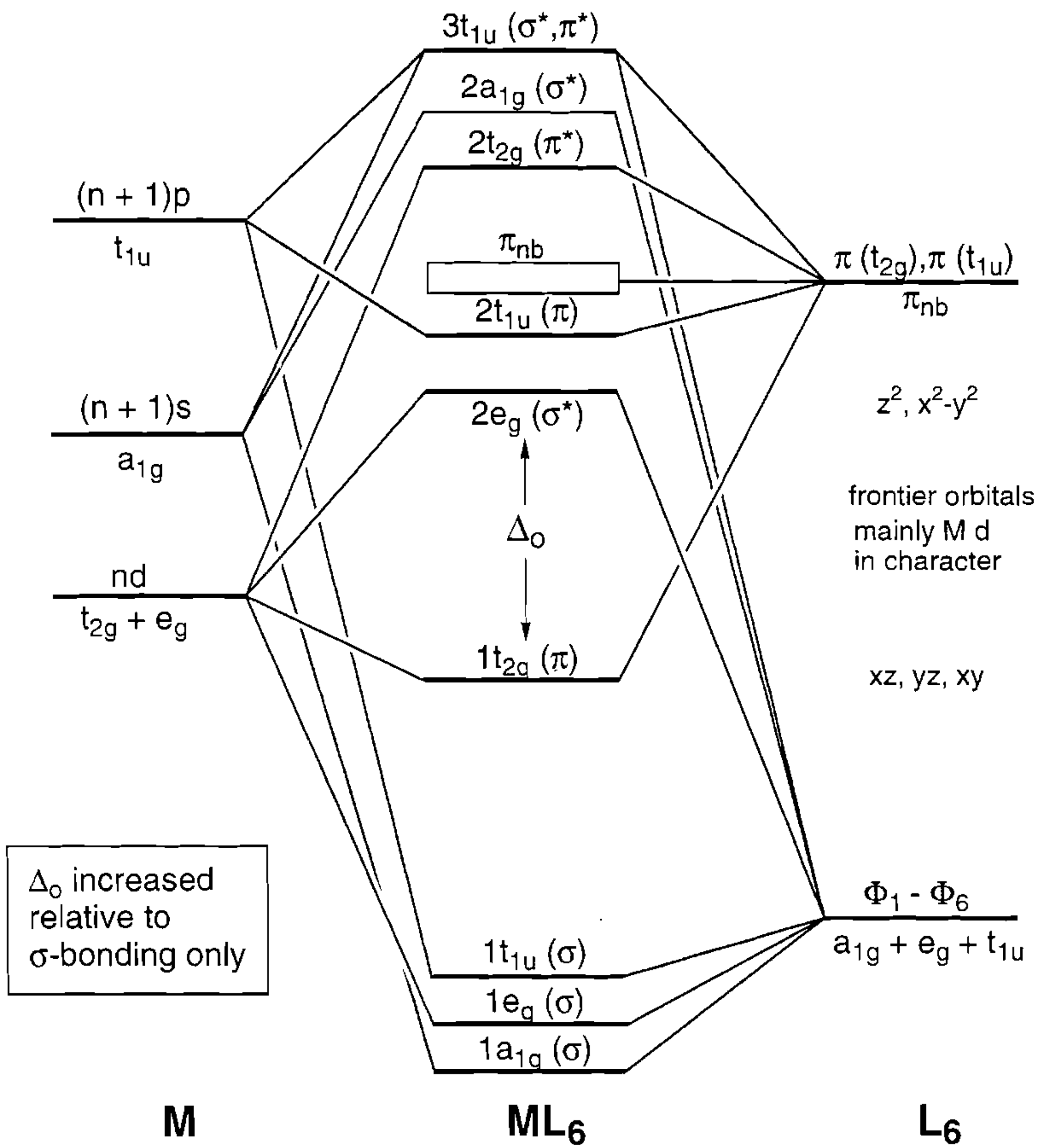
Case 1. Lπ orbitals filled and more stable than dπ orbitals (L is a π-donor)



prime example

F^-

Case 2. Lπ orbitals vacant and less stable than dπ orbitals
(L is a π-acceptor)



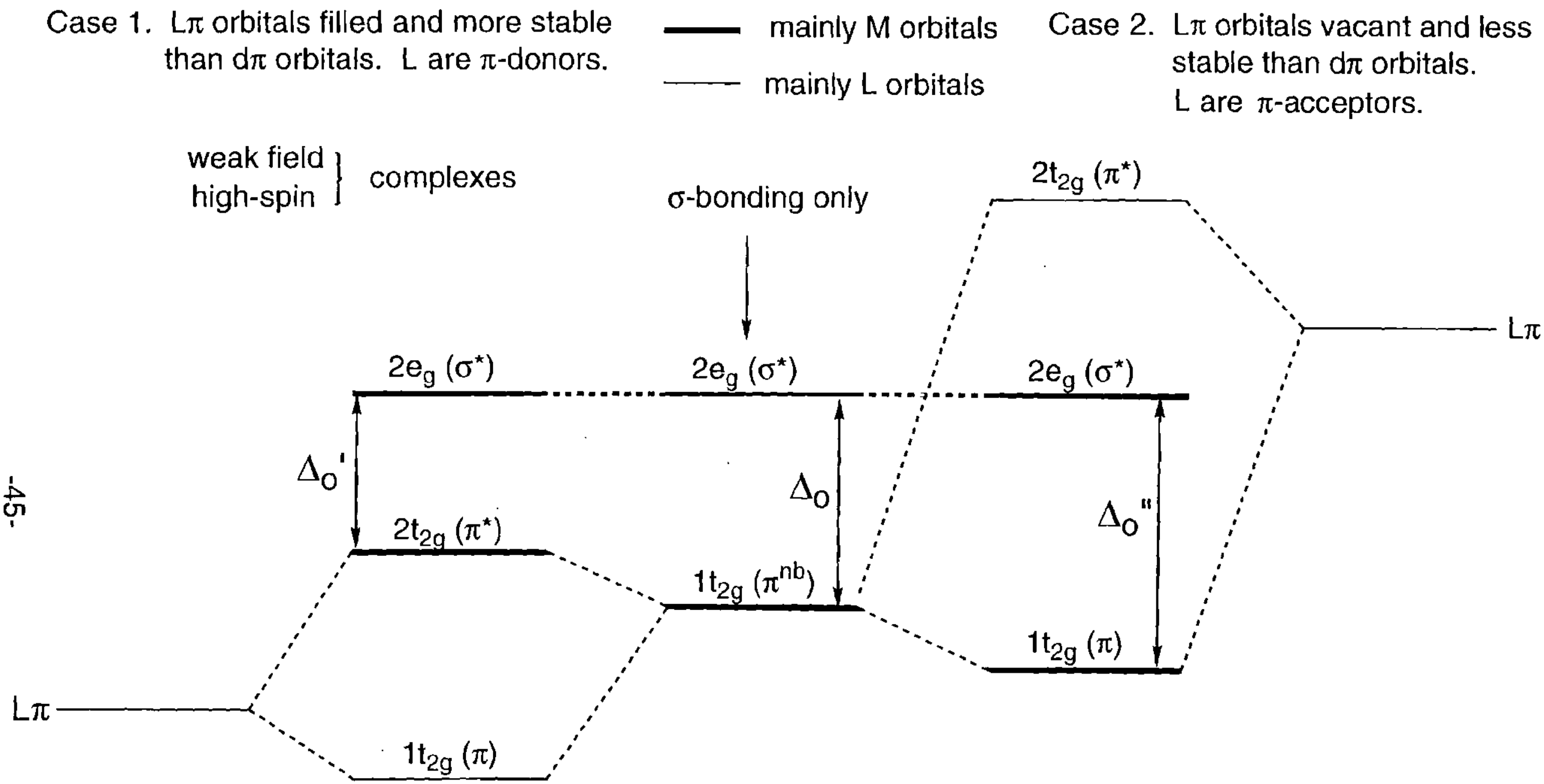
prime example

CO

Important Cases of d-Orbital Splittings in Octahedral Complexes

Case 1. Lπ orbitals filled and more stable than dπ orbitals. L are π-donors.

Case 2. Lπ orbitals vacant and less stable than dπ orbitals. L are π-acceptors.



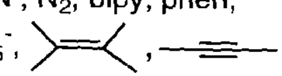
$\Delta_o' < \Delta_o < \Delta_o''$

$L_{\pi\text{-donor}}$ = F^-, Cl^-, Br^-, I^-, H_2O, OH^-, RS^-, S^{2-}, NCS^-, NCO^-, ...

(virtually any ligand which, after forming M-L σ-bonds, has lone pairs)

L_σ = NR_3

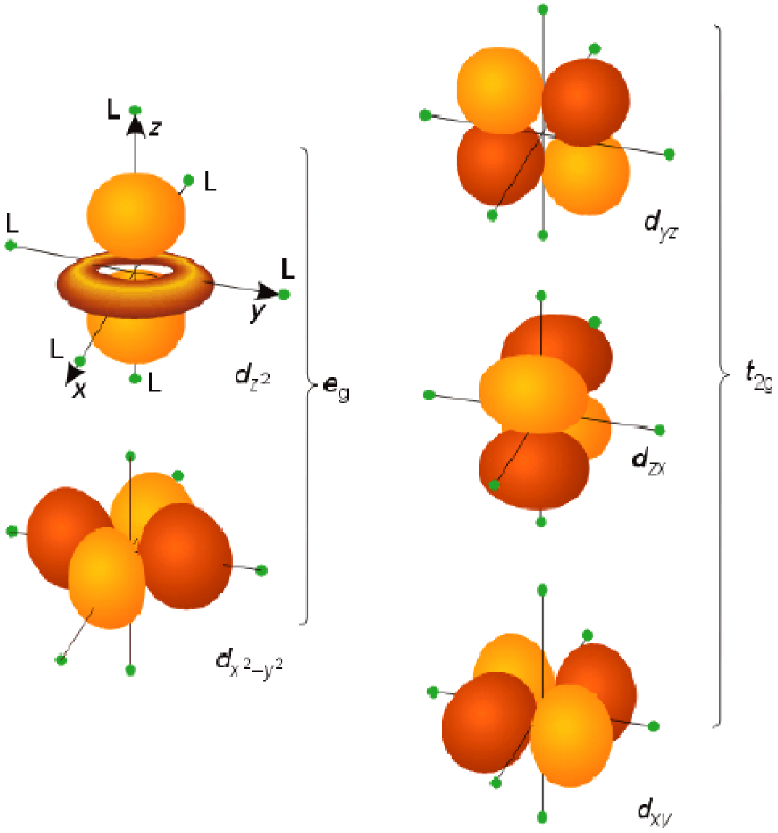
$\underbrace{L_\sigma = NR_3 \qquad L_{\pi\text{-acceptor}}}_{PR_3}$

$L_{\pi\text{-acceptor}}$ = CO, NO, CN^-, N_2, bipy, phen, RNC, $C_5H_5^-$, 

(virtually any ligand with vacant π* MO's)

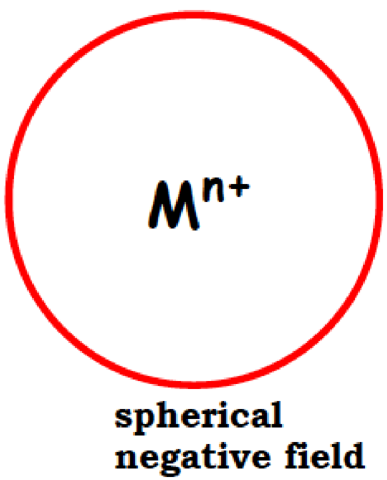
CFT-Assumptions

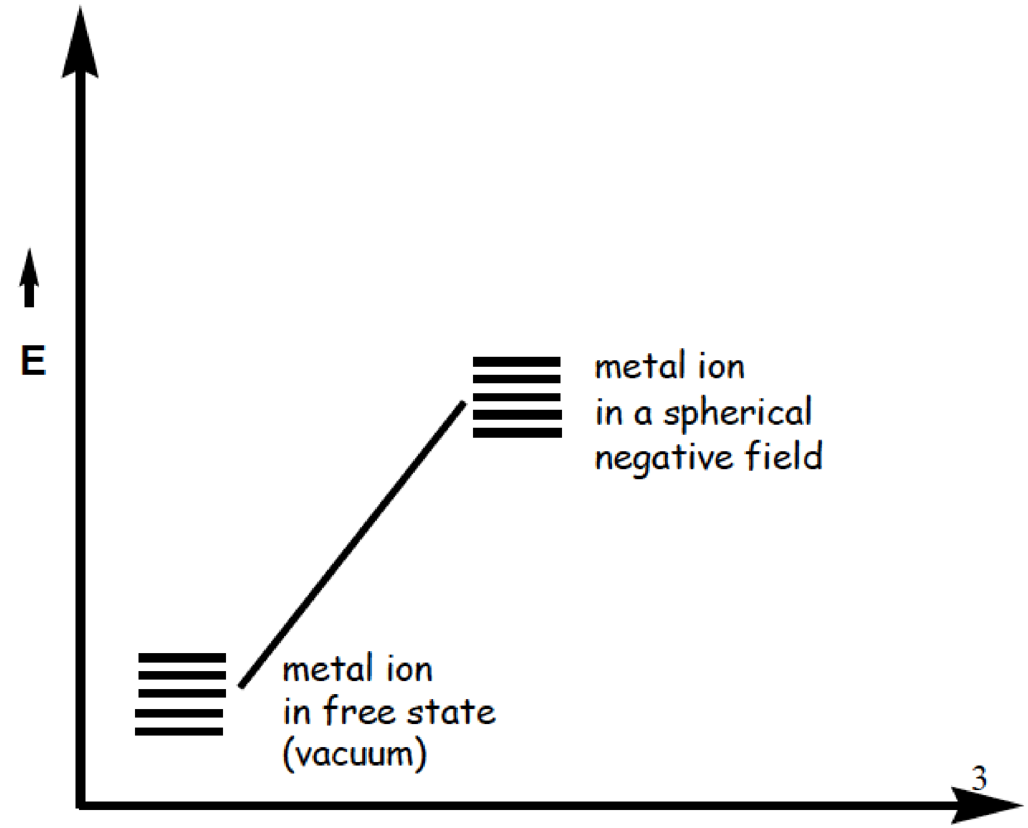
- The interactions between the metal ion and the ligands are purely electrostatic (ionic).
- The ligands are regarded as point charges
- If the ligand is negatively charged: ion-ion interaction. If the ligand is neutral : ion-dipole interaction
- The electrons on the metal are under repulsive from those on the ligands
- The electrons on metal occupy those d-orbitals farthest away from the direction of approach of ligands



Symmetric Field

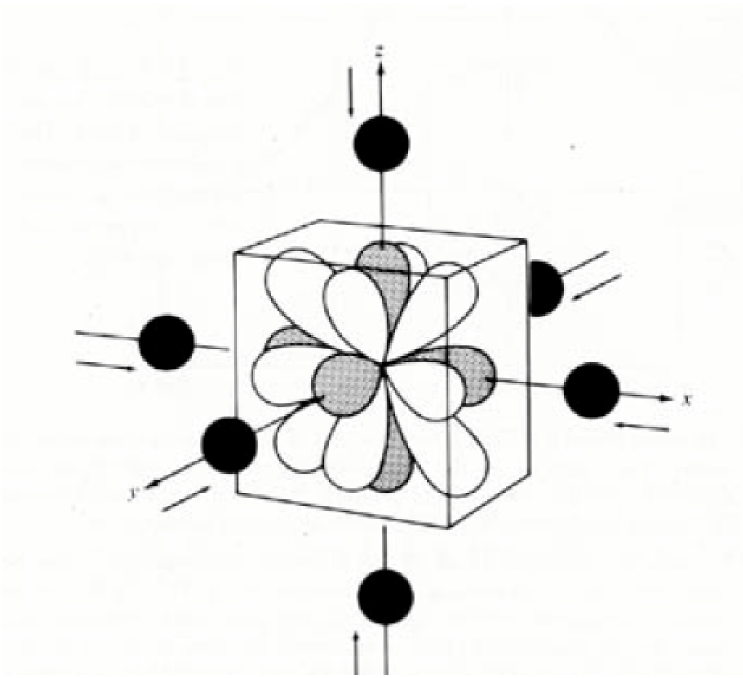
- The 5d orbitals in an isolated gaseous metal are degenerate.
- If a spherically symmetric field of negative charges is placed around the metal, these orbitals remain degenerate, but all of them are raised in energy as a result of the repulsion between the negative charges on the ligands and in the d orbitals.

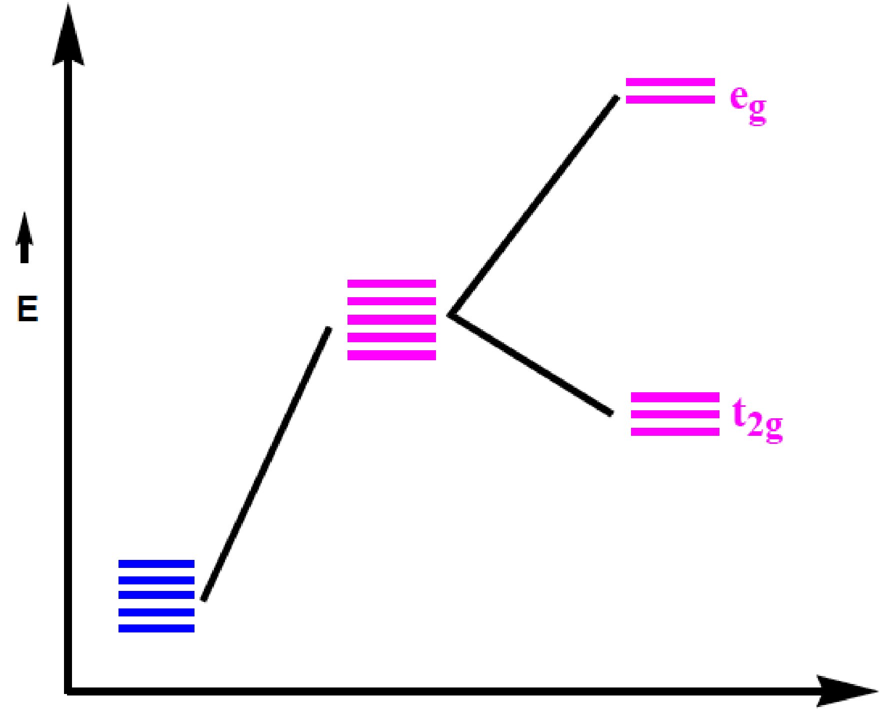




Octahedral Field

•If rather than a spherical field, discrete point charges (ligands) are allowed to interact with the metal, the degeneracy of the d orbitals is removed (or, better said, lifted). The splitting of d orbital energies and its consequences are at the heart of crystal field theory.





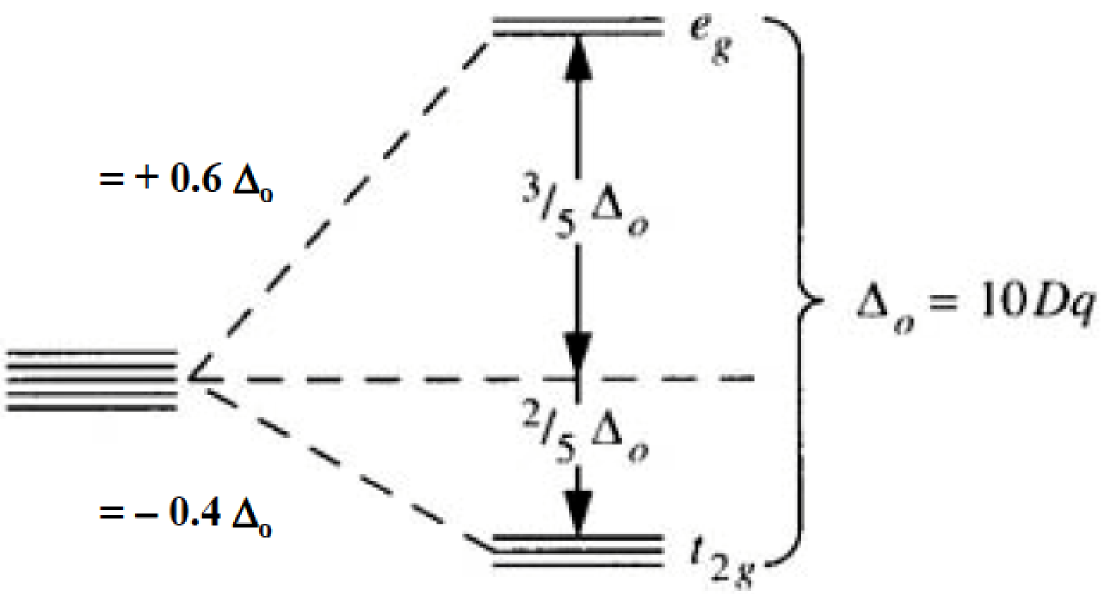
•Not all d orbitals will interact to the same extent with the six point charges located on the +x, -x, +y, -y, +z and -z axes respectively.

•The orbitals which lie along these axes (i.e. x^2-y^2, z^2) will be destabilized more that the orbitals which lie in-between the axes (i.e. xy, xz, yz).

CFT-Octahedral Complexes

•For the Oh point group, the x^2-y^2, z^2 orbitals belong to the E_g irreducible representation and xy, xz, yz belong to the T_{2g} representation.

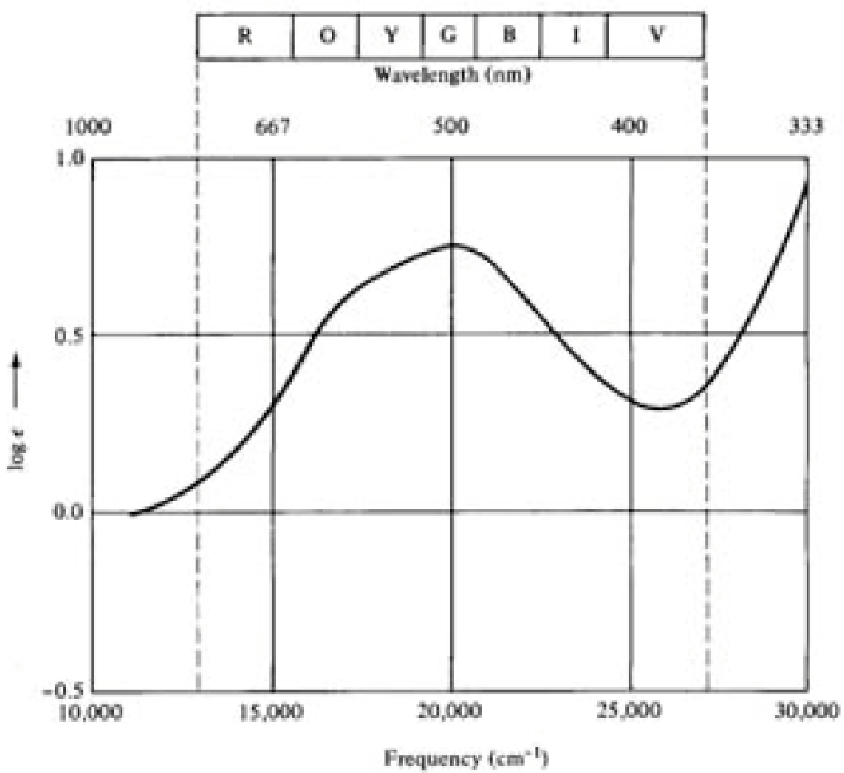
•The extent to which these two sets of orbitals are split is denoted by Δ_o or alternatively 10Dq. As the **baricenter** must be conserved on going from a spherical field to an octahedral field, the t_{2g} set must be stabilized as much as the e_g set is destabilized.



Chem Wiki UC Davis

Illustration of CFSE

$[Ti(H_2O)_6]^{3+}$: a d^1 complex and the e^- occupies the lowest energy orbital, i.e. one of the three degenerate t_{2g} orbitals. The purple colour is a result of the absorption of light which results in the promotion of this t_{2g} electron into the e_g level. $t_{2g}^1e_g^0 \rightarrow t_{2g}^0e_g^1$



The UV-Vis absorption spectrum reveals that this transition occurs with a maximum at 20300 cm^{-1} which corresponds to Δ_o 243 kJ/mol.

(1000 cm^{-1} = 11.96 kJ/mol or

2.86 kcal/mol or

0.124 eV.)

Typical Δ_0 values are of the same order of magnitude as the energy of a chemical bond.

- **What happens for more than 1 electron in d orbitals?**
- **The electron-electron interactions must be taken into account.**
- **For d^1-d^3 systems:** Hund's rule predicts that the electrons will not pair and occupy the t_{2g}set.
- **For d^4-d^7 systems (** there are two possibilities): Either put the electrons in the t_{2g} set and therefore pair the electrons (**low spin case** or **strong field situation**. Or put the electrons in the e_g set, which lies higher in energy, but the electrons do not pair (**high spin case** or **weak field situation)**.
- Therefore, there are two important parameters to consider: **The Pairing energy (P)**, and **the e_g - t_{2g} Splitting (referred to as Δ_0, 10Dq or CFSE)**
- For both the high spin (h.s.) and low spin (l.s.) situations, it is possible to compute the **CFSE.**

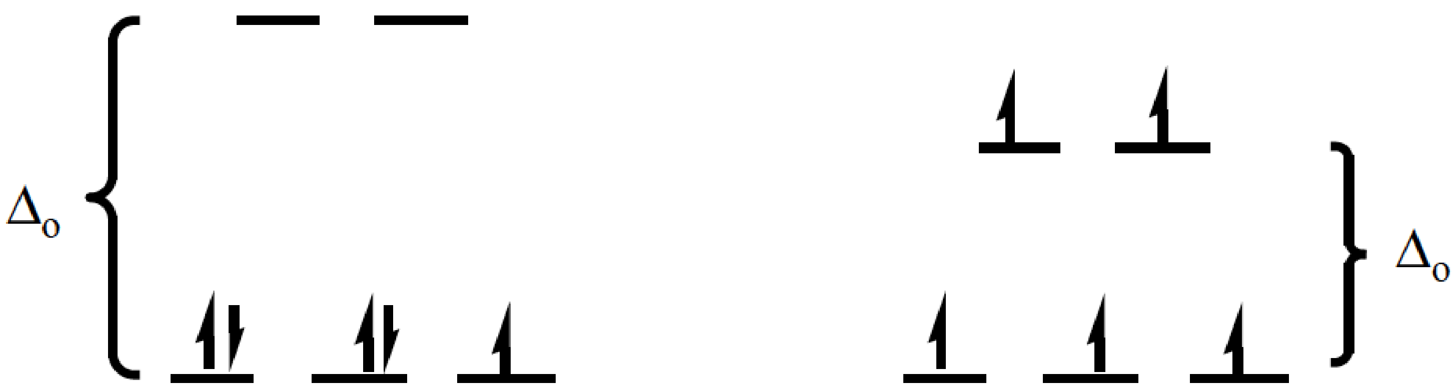
For an octahedral complex, CFSE

$$\boxed{= -0.4 \times n(t_{2g}) + 0.6 \times n(e_g)\ \Delta_o}$$

Where, $n(t_{2g})$ and $n(e_g)$ are the no. of electrons occupying the respective levels

If CFSE is very large, pairing occurs (i.e. CFSE > P)
If CFSE is rather small, no pairing occurs (i.e P > CFSE)

d^5 system



Case I results in LS complex

Case II results in HS complex

Δ_o is dependent on:

- *Nature of the ligands*
- *The charge on the metal ion*
- *Whether the metal is a 3d, 4d, or 5d element*

Ligands which cause a small splitting are ***Weak field ligands*** (CFSE in the range 7000 - 30000 cm^{-1}) and those cause a large splitting are ***Strong field ligands*** (CFSE typically > 30000 cm^{-1})

Spectrochemical Series

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-$, $F^- <$ urea, $OH^- <$ ox, $O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^-$, $C_6H_5^- < CN^- < CO$.

$[CrCl_6]^{3-}$	13640 cm^{-1}	163 kJ/mol
$[Cr(H_2O)_6]^{3+}$	17830	213
$[Cr(NH_3)_6]^{3+}$	21680	314
$[Cr(CN)_6]^{3-}$	26280	314

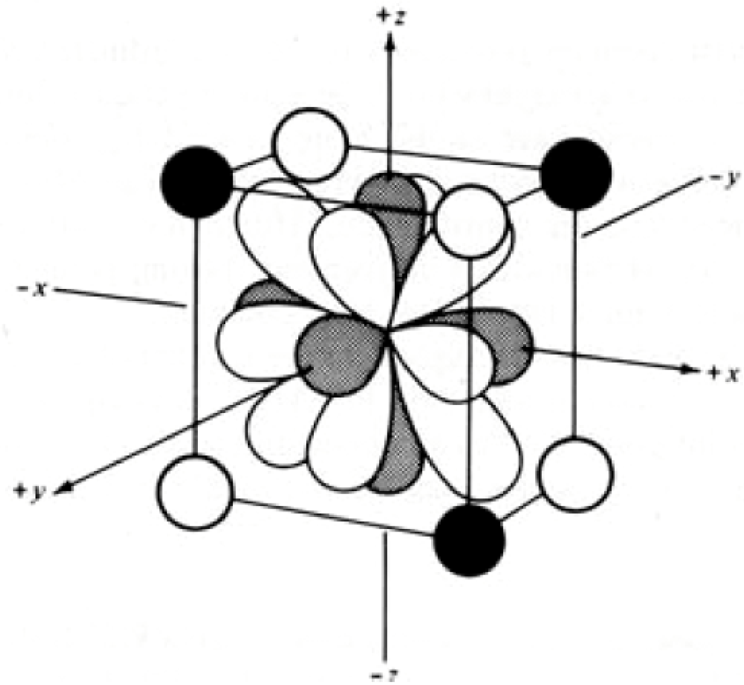
$[Co(NH_3)_6]^{3+}$	24800 cm^{-1}	163 kJ/mol
$[Rh(NH_3)_6]^{3+}$	34000	213
$[Ir(NH_3)_6]^{3+}$	41000	314

Tetrahedral Field- Considerations

Imagine a tetrahedral molecule inside a cube with metal ions in the center of the cube. The ligands occupy the four alternate corners of the cube leaving the rest four corners empty.

The two ‘e’ orbitals point to the center of the face of the cube while the three ‘t_2’ orbitals point to the center of the edges of the cube.

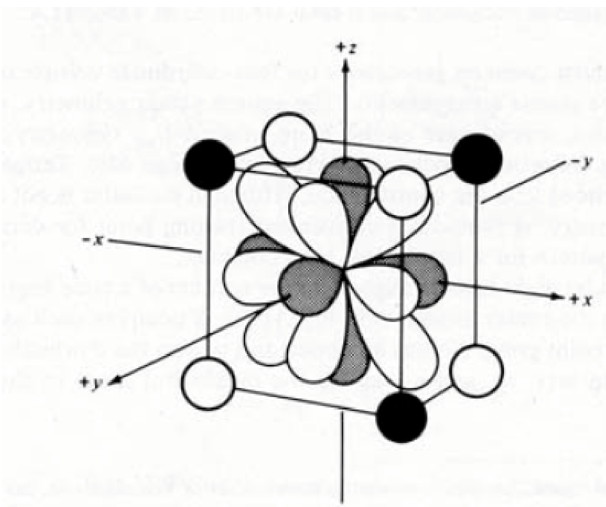
Therefore, the angle between the e-orbitals, metal and ligand is one-half of the tetrahedra angle, i.e. **109°28’ / 2 = 54°44’**. But the angl between the t_2-orbitals, metal and ligand is one-third of the tetrahedral angle, i.e. **109°28 / 3 = 35°16’**.

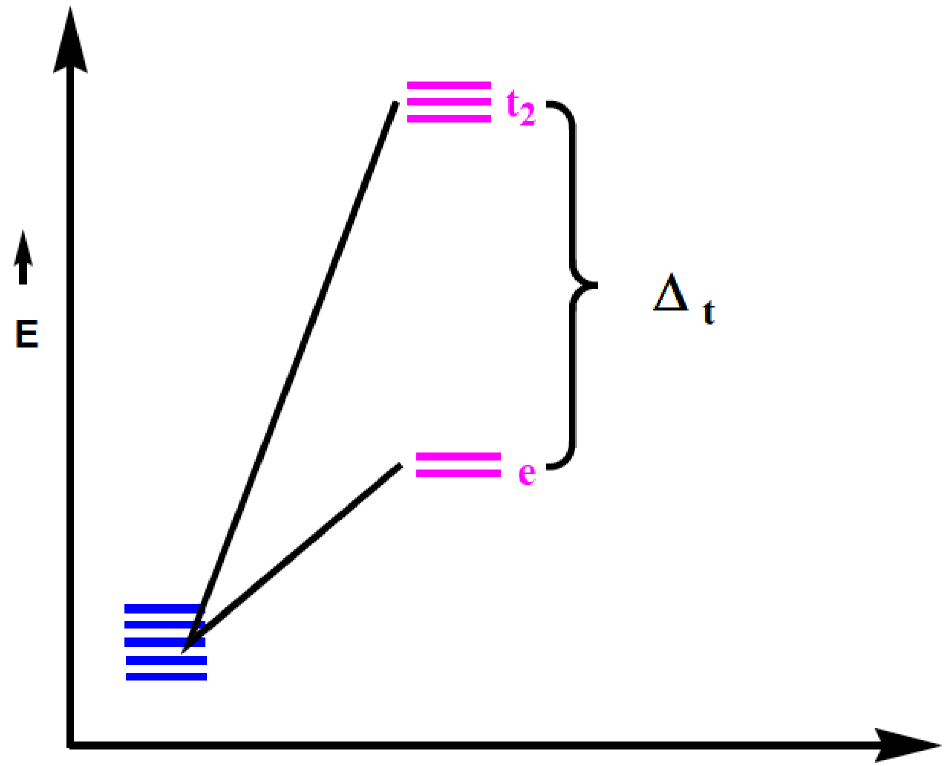


Thus the t_2 orbitals are nearer to the direction of approach of the ligands than the e orbitals.

Hence, t_2 orbitals have higher energy compared to e-orbitals

Tetrahedral Field





$$\Delta_t < \Delta_o$$

$$\Delta_t = 4/9\ \Delta_o$$

There are only 4 ligands in the tetrahedral complex, and hence the ligand field is roughly 2/3 of the octahedral field.

The direction of ligand approach in tetrahedral complex does not coincide with the d-orbitals. This reduces the field by a factor of 2/3. Therefore Δ_t is roughly 2/3 x 2/3 = 4/9 of Δ_o

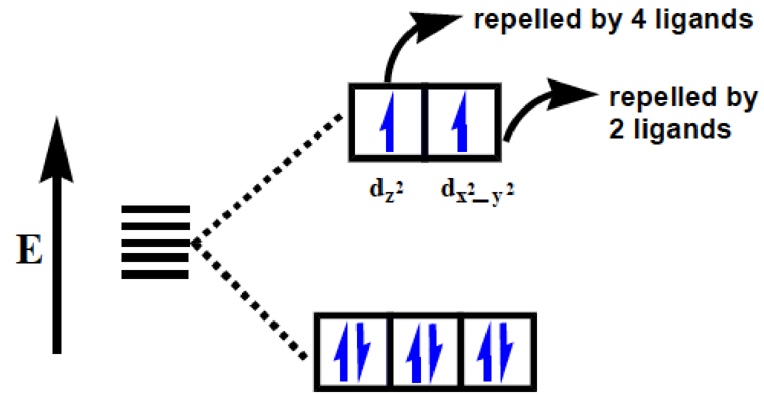
As a result, **all tetrahedral complexes are high-spin** since the CFSE is normally smaller than the paring energy.

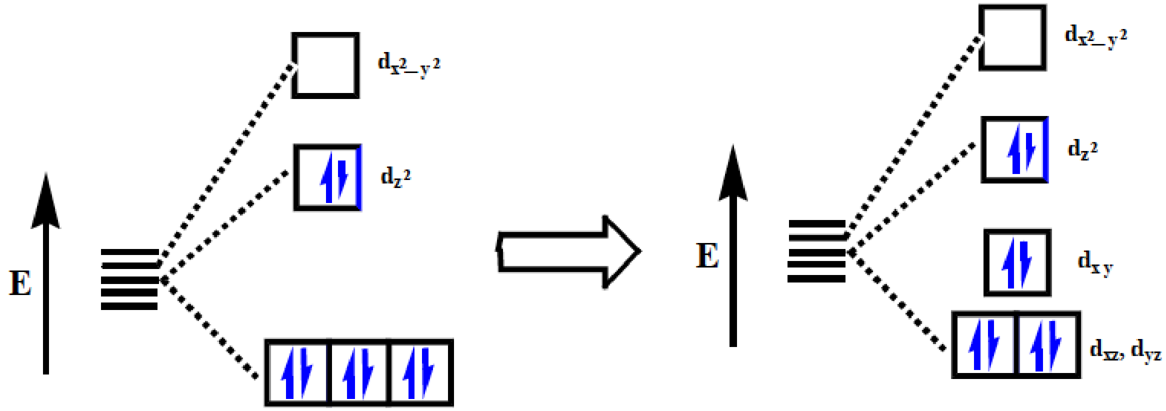
Hence low spin configurations are rarely observed. Usually, if a very strong field ligand is present, the square planar geometry will be favored.

Special case of d^8 Octahedral

Examples:

Ni^{2+}, Pd^{2+}, Pt^{2+}, Cu^{3+}, Ag^{3+}, Au^{3+}



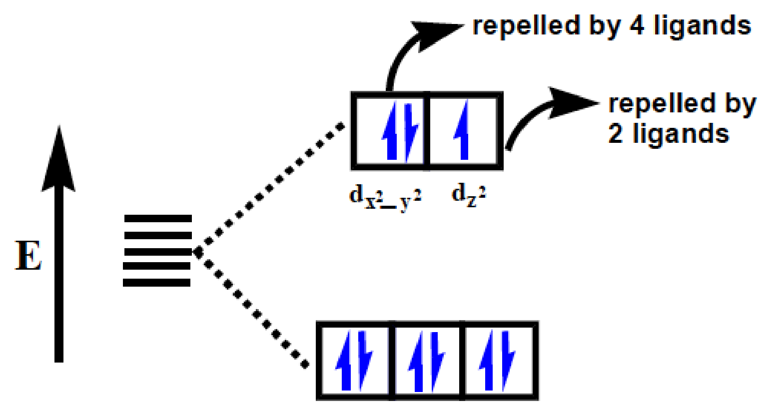


Square-planar complex is formed ; attempts to form octahedral complexes become impossible

Special case II
Jahn-Teller Distortion

If bot the e_g orbitals are symmetrically filled - all ligands are repelled equally. **Result:** regular octahedron

If **asymmetrically** filled - some ligands are repelled more than the other . **Result:** Distorted octahedron



Consider e_g configuration: $(d_{z^2})^1\ d_{x^2-y^2})^2$

Ligands along x, -x, y, -y will be repelled more and bonds elongated. i.e. the octahedron will be compressed along the z axis.

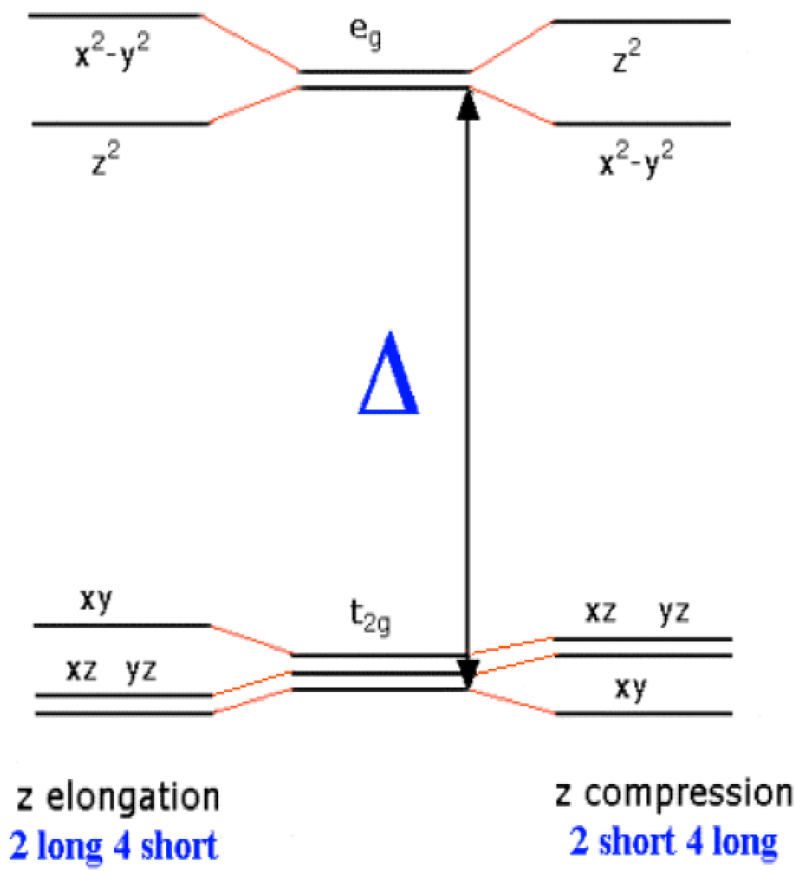
Consider e_g configuration: $(d_{z^2})^2\ d_{x^2-y^2})^1$

Ligands along z, -z will be repelled more and bonds elongated. i.e. the octahedron will be elongated along the z axis.

The Jahn-Teller Theorem was published in 1937 and states:

> "any non-linear molecular system in a degenerate electronic state will be unstable and will undergo distortion to form a system of lower symmetry and lower energy thereby removing the degeneracy"

The e_g point along bond axes. The effect of JT distortions is best documented for Cu(II) complexes (with 3e in e_g) where the result is that most complexes are found to have elongation along the z-axis.



Some examples of Jahn-Teller distorted complexes

$CuBr_2$	4 Br at 240pm 2 Br at 318pm
$CuCl_2.2H_2O$	2 O at 193pm 2 Cl at 228pm 2 Cl at 295pm
$CsCuCl_3$	4 Cl at 230pm 2 Cl at 265pm
CuF_2	4 F at 193pm 2 F at 227pm
$CuSO_4.4NH_3.H_2O$	4 N at 205pm 1 O at 259pm 1 O at 337pm
K_2CuF_4	4 F at 191pm 2 F at 237pm
CrF_2	4 F at 200pm 2 F at 243pm
$KCrF_3$	4 F at 214pm 2 F at 200pm
MnF_3	2 F at 209pm 2 F at 191pm 2 F at 179pm

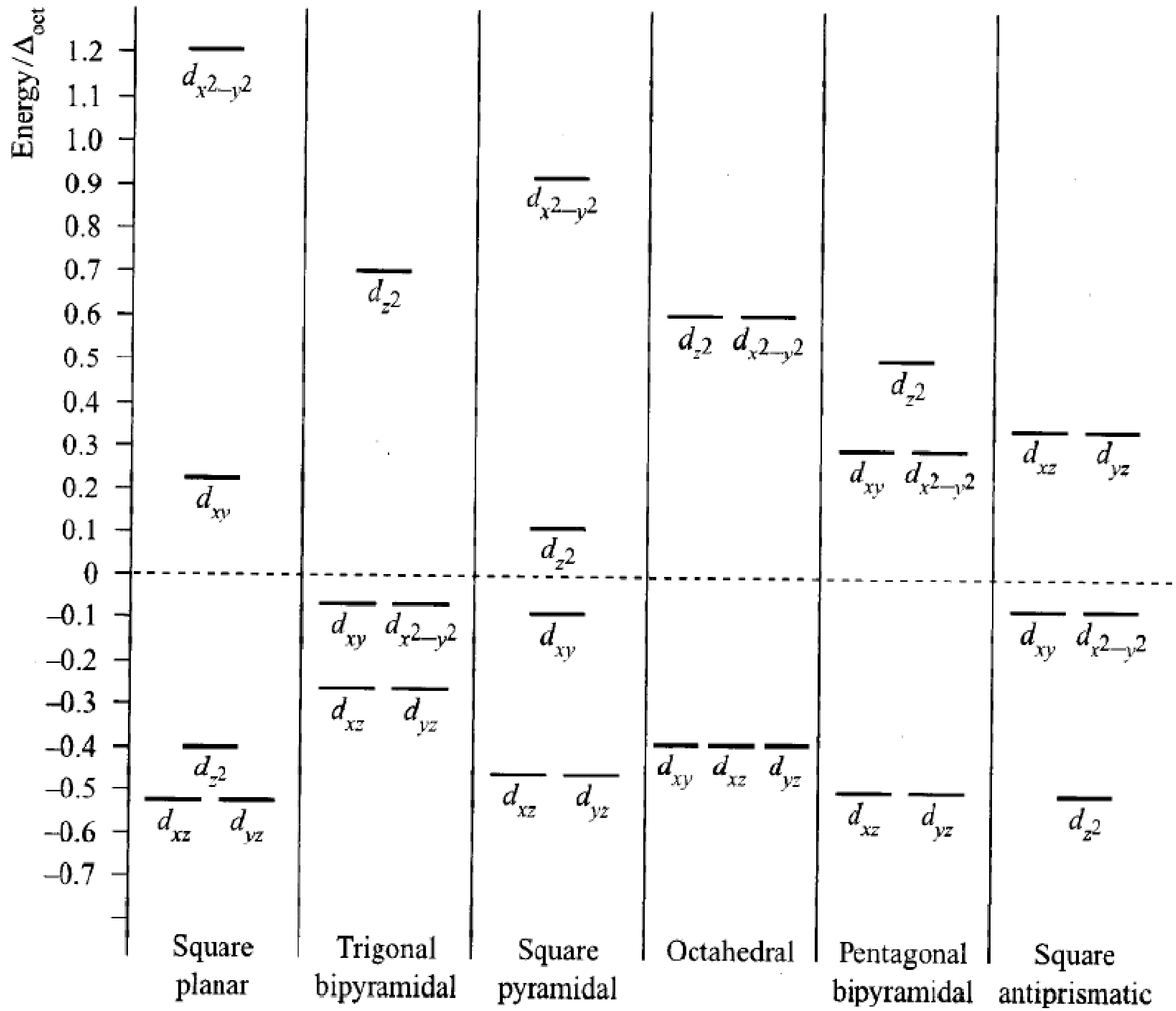
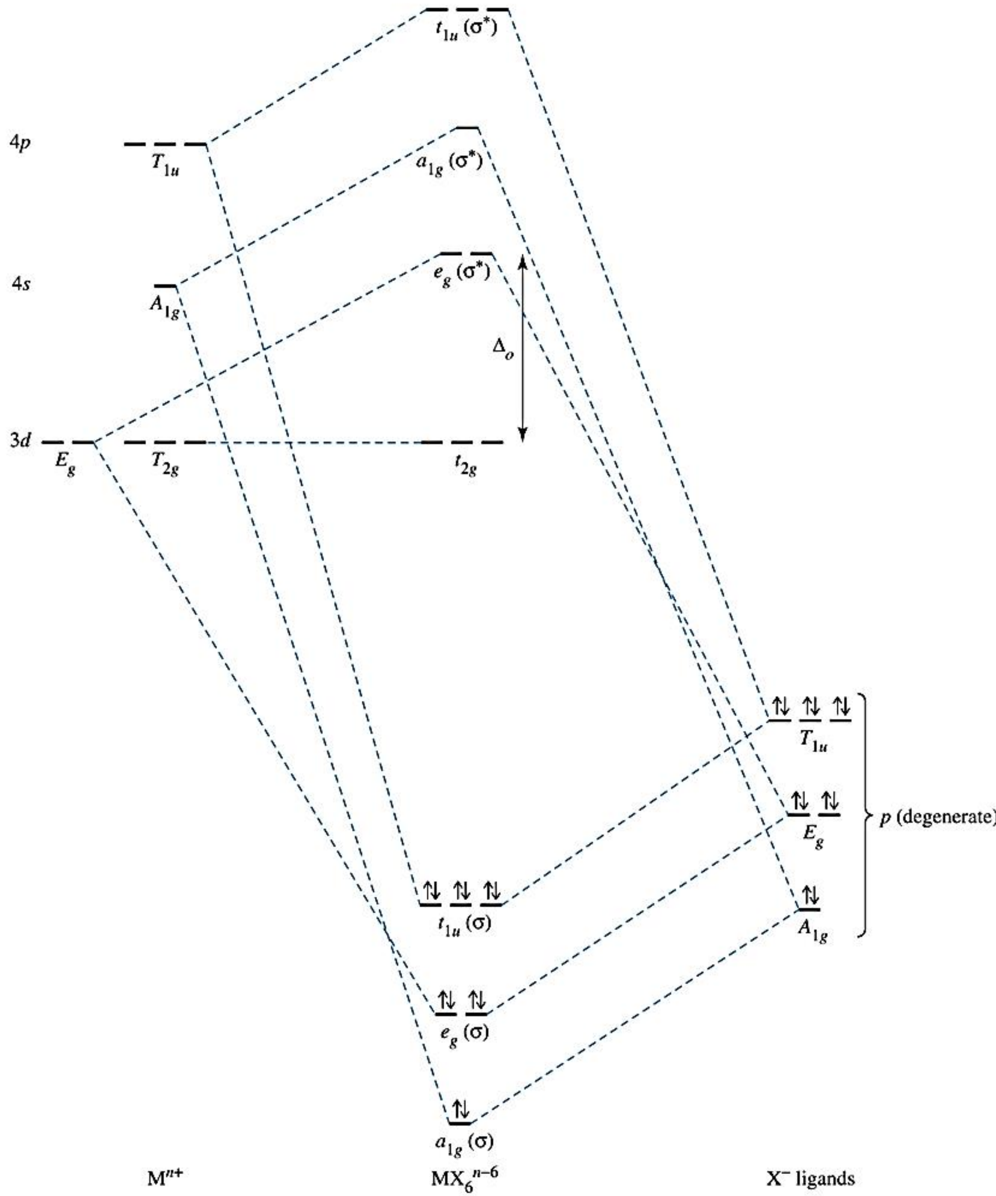


Figure 2 Crystal field splittings of d orbitals


t_{1u} (σ^*)
4p
T_{1u}
a_{1g} (σ^*)
4s
A_{1g}
e_g (σ^*)
Δ_o
3d
E_g
T_{2g}
t_{2g}
T_{1u}
E_g
p (degenerate)
A_{1g}
t_{1u} (σ)
e_g (σ)
a_{1g} (σ)
M^{n+}
MX_6^{n-6}
X^- ligands