Topics

Coordination Compounds

- Lewis Acid/Base Adducts
- Definitions
  - complexes, ligands, coordination number
- Coordination Number and Shapes
- Ligands
  - Isomerism
    - linkage, geometric, optical
  - Sigma and pi bonding
- MO Theory and Crystal Field Theory
- MO Theory and Ligand Field Theory

Coordination Complexes

- Working model proposed by Werner
  - formerly known as Werner complexes
  - awarded Nobel prize in chemistry 1913
  - Recognized the bonding between ligands and metals rather than simple ionic solids
  - Proposed coordination number using physical and chemical observation
- "complexes" originally because they did not conform to existing models
- e.g. colbalt(III) chloride-ammonia

Colbalt(III) Chloride-Ammonia Complexes

Complex	Colour	Name	Ag^+ Rx	Structure
$CoCl_3 \cdot 6NH_3$	Yellow	Luteo	3 AgCl	$\left\{ \begin{array}{c} NH_3 \\ H_3N \cdots Co \cdots NH_3 \\ H_3N \quad NH_3 \\ NH_3 \end{array} \right\} 3Cl$
$CoCl_3 \cdot 5NH_3$	Purple	Purpureo	2 AgCl	$\left\{ \begin{array}{c} Cl \\ H_3N \cdots Co \cdots NH_3 \\ H_3N \quad NH_3 \\ NH_3 \end{array} \right\} 2Cl$
$CoCl_3 \cdot 4NH_3$	Green	Praseo	1 AgCl	$\left\{ \begin{array}{c} Cl \\ H_3N \cdots Co \cdots NH_3 \\ H_3N \quad NH_3 \\ Cl \end{array} \right\} Cl$
$CoCl_3 \cdot 4NH_3$	Violet	Violeo	1 AgCl	$\left\{ \begin{array}{c} Cl \\ H_3N \cdots Co \cdots Cl \\ H_3N \quad NH_3 \\ NH_3 \end{array} \right\} Cl$

Lewis Acid-Lewis Base Adducts

- Lewis acid – species (atom or molecule) capable of accepting electron density
- Lewis base – species (atom or molecule) capable of donating electron density
- Adducts – the resulting species formed by the combination of a Lewis acid and Lewis base

$$A + B: \rightarrow A:B$$

- in transition metal complexes:
  - M – central metal atom is Lewis Acid
  - L – various species act as Lewis bases and donate electron density to the metal

Definitions

- Ligands
  - an ion or molecule which donates electron density to a metal atom/ion to form a complex
- Coordination Complex
  - a central metal atom/ion and its set of ligands
  - often an ion itself
- Coordination Compounds
  - a neutral species made up in some part of a complex
  - often the salt of a coordination complex
- Coordination Number
  - the number of ligands in the primary or inner shell of ligands

Inner Sphere/Outer Sphere

- Inner sphere complex is the species formed only by the ligands directly attached to the central metal atom/ion
- aka primary coordination sphere
- Outer sphere complex is the same species expanded to include subsequent layers which interact at a distance with the complex
  - could include an ion pair electrostatically interacting with the complex
  - or solvent molecules oriented by dipole-dipole interactions with the inner sphere complex
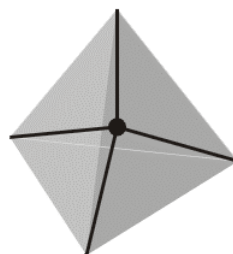
Coordination Numbers (CN)

- In General CN Determined by
  1. Size of central metal ion/atom
  2. Steric interactions between ligands
  3. Electronic interactions
- Examples:
  - Large radii atoms for n=5,6 have high CN
  - Bulky ligands tend to prefer reduced coordination number
  - Lewis bases contribute e$^-$ density to the metal center, low "d" metals can take in more e$^-$ density.
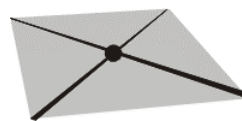
Coordination Numbers

- CN 2
  - Typically large ligands or high d metals
  - Cu, Ag, Au species
  - $Hg(CH_3)_2$ – dimethyl mercury

Coordination Number: 4

– Very popular coordination number

– Tetrahedral or square planar geometries

– Tetrahedral

- Formed when steric crowding is important
  – Small central atom, large ligands
- High oxidation state, low d metals

4 Tetrahedral complex, T_c

– Square Planar

- Formed when planarity is important
  – π bonding ligands, lining up orbitals
- Favoured with d^8 metals
  – Ni^{2+}, Rh^{1+}, Ir^{1+}, Pt^{2+}, Pd^{2+}, Au^{3+}
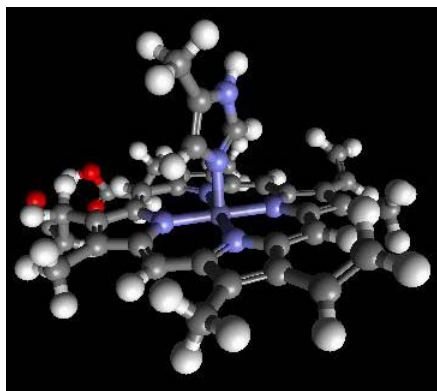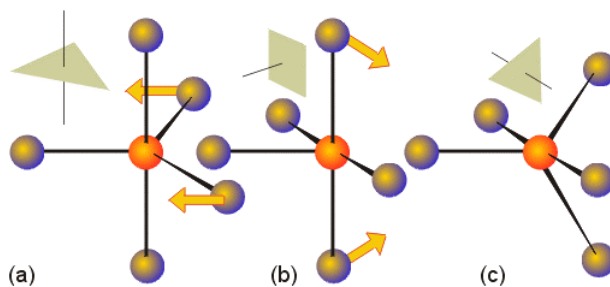
6 Square-planar complex, D_{4h}

Coordination Number: 5

- Less common than 4 or 6
- Two types:
  - Trigonal bipyramidal
    - spacious arrangement Square Pyramidal
    - Biologically important (myoglobin)

- Very similar in energy, allows fluxionality
  - Berry Pseudorotation

Berry Pseudorotation



(a)   (b)   (c)

Coordination Number: 6

- Very common coordination number
- Found for d^0 to d^9 metals
- Highly symmetric arrangementin its undistorted form
- Often study structures as a function of their distortion from octahedral geometry
  - Particularly tetragonal distortions
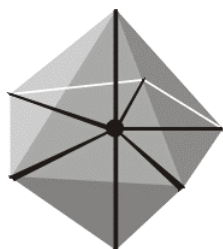   - (d^9 eg Cu^{2+})
  - Also trigonal prismatic species
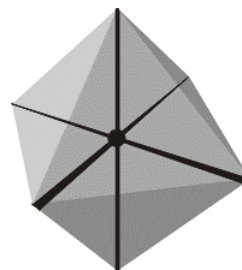
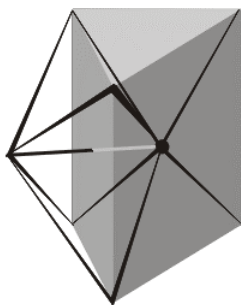**10** Octahedral complex, O_h

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Distortions from Octahedral Geometry

- Compression or elongation of opposite vertices leads to tetragonal distortion (a) and (b)
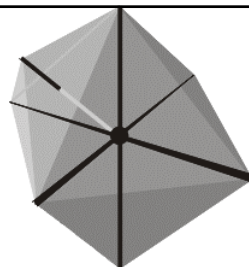- Also rhombic (c) and trigonal distortions (d)
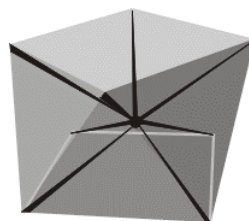
(a)   (b)

(c)   (d)
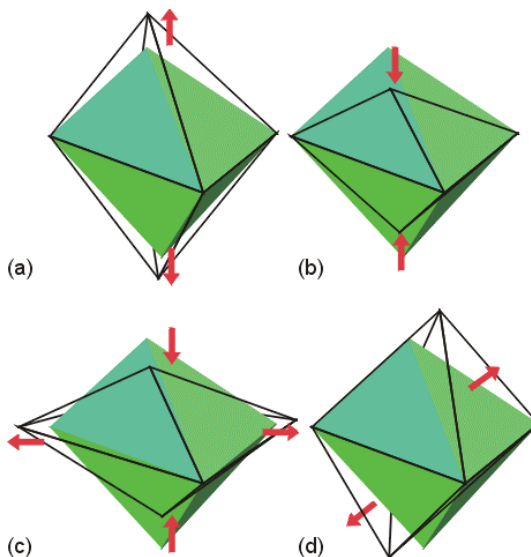
Higher Coordination Numbers

13 Pentagonal-bipyramidal complex, D_{5h}
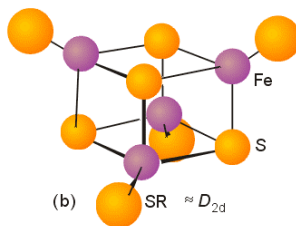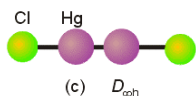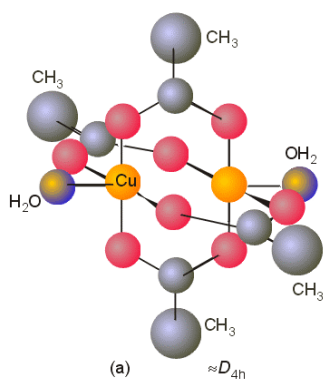
14 Capped octahedral complex

15 Capped trigonal prism

17 Square-antiprismatic complex

Polymetallic Complexes
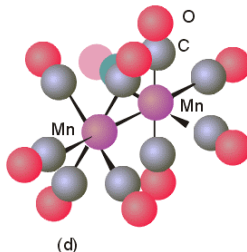
Increasingly interesting for nanoscale properties, particularly metal clusters.
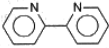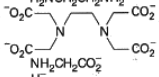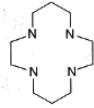
(a) $\approx D_{4h}$ — CH_3, CH_3, Cu, OH_2, H_2O, CH_3, CH_3

(b) Fe, S, SR $\approx D_{2d}$

(c) Cl, Hg, $D_{\infty h}$

(d) O, C, Mn, Mn

Ligands

- Lewis Base: requires "excess" electron density
  - P species: phosphines (PR_xH_{3-x})
  - Halogens
  - N species: amines, Nitro
  - O species: H_2O (aqua/aquo), OR^-
  - S species: SR^-, SO_x
  - Organics : aromatics, olefins, alkyls, carbenes

See Table 7.1 p. 220 Shriver and Atkins

Table 7.1 Typical ligands and their names

Name	Formula	Abbreviation	Classification*
Acetylacetonato	$(CH_3COCHCOCH_3)^-$	acac	B(O)
Ammine	NH_3		M(N)
Aqua	OH_2		M(O)
2,2-Bipyridine		bipy	B(N)
Bromo	Br^-		M(Br)
Carbonato	CO_3^{2-}		M(O)
Carbonyl	CO		M(C)
Chloro	Cl^-		M(Cl)
Cyano	CN^-		M(C)
Diethylenetriamine	$NH(C_2H_4NH_2)_2$	dien	T(N)
Ethylenediamine	$H_2NCH_2CH_2NH_2$	en	B(N)
Ethylenediaminetetraacetato		edta	S(N,O)
Glycinato	$NH_2CH_2CO_2^-$	gly	B(N,O)
Hydrido	H^-		M
Hydroxo	OH^-		M(O)
Maleonitriledithiolato		mnt	B(S)
Nitrilotriacetato	$N(CH_2CO_2^-)_3$	nta	Te(N,O)
Oxo	O^{2-}		M
Oxalato	$C_2O_4^{2-}$	ox	B(O)
Nitrito	NO_2^-		M(O)
Tetraazacyclotetradecane		cyclam	Te(N)
Thiocyanato	SCN^-		M(S)
Isothiocyanato	SCN^-		M(N)
2,2',2''-Triaminotriethylamine	$N(C_2H_4NH_2)_3$	trien	Te(N)

*M: monodentate, B: bidentate, T: tridentate, Te: tetradentate, S: sexidentate. The letters in parentheses identify donor atoms.

Ligand Names

- Anionic ligands end in "o"
  - Bromo, chloro, carbonato
- Neutral species use only name of the molecule or group
  - Ethylenediamine
  - phosphine
- Other common names:
  - Aquo/aqua
- Bridging Ligands denoted by μ (mu)
- Multiple bonding atoms denoted by η (hapto)

Nomenclature

- General Rules
  - Name ligands in alphabetical order
  - Follow ligands with metal using using oxidation number in parentheses
  - Use metal + "ate" for anionic complexes
  - Prefix Ligands with standard multiplicity:
    - Mono,di, tri, tetra, penta, hexa etc
    - When ligands include standard multipliers use bis, tris, tetrakis

Nomenclature Examples

- Sodium hexacyanoferrate(III) ^{3Na}
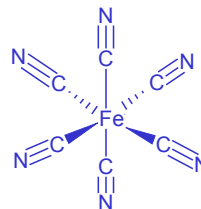
- μ-oxo-bis(pentamminechromium(III))
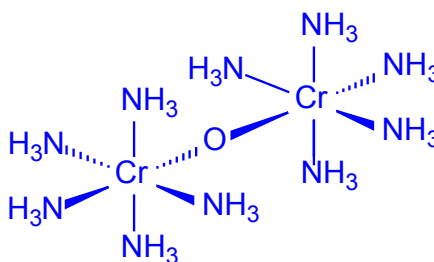
Chemical Formulae

- Enclose the formula in square brackets
- List Metal centre first
- Then list anionic ligands
- Then list neutral ligands

- *e.g.* diamminedichloroplatinum(II)

$$[PtCl_2(NH_3)_2]$$

Chelation
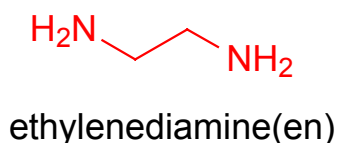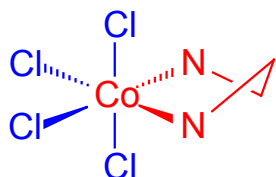
- Arises from a ligand capable of binding to a metal centre with two or more atoms simultaneously (for example a bidentate ligand)
- when a multidentate ligand forms a ring involving the central metal atom

ethylenediamine(en)

Chelation and Bite Angle

- Geometry of complexes can be limited by the "bite angle" of a chelating ligand
  - The carbon chain or other backbone of a chelate ligand restricts the angle spanned by the bonding atoms
  - This can distort or drive a complex geometry into a particular shape
  - i.e. conversion from octahedral to trigonal prism

O_h to Trigonal Prism to ease Bite Angle
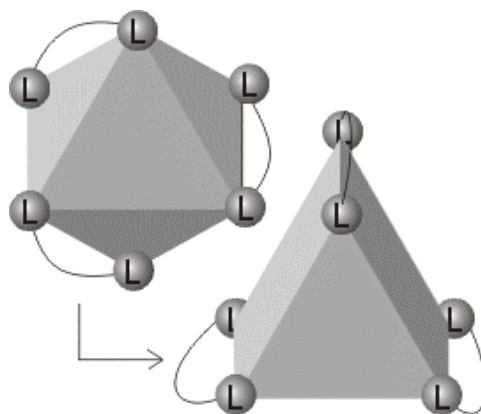
32

Isomerism

- Three types
  - Linkage
  - Geometric
  - Optical

Linkage Isomerism

- Arises from ambidentate ligands
  - Some ligands have more than one site of potential Lewis basicity
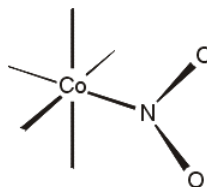   - Thiocyano (SCN$^-$)
      - Thiocyanato = S bonded, isothiocyanato = N bonded
    - Nitro/Nitrito (NO$_2^-$)
      - N bonded or O bonded respectively

- Results in entirely different compound

Linkage Isomerism
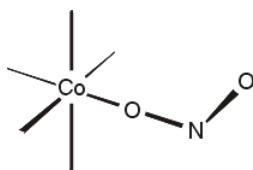
25 Nitrito ligand

26 Nitro ligand

Geometric Isomerism

- Due to arrangement of ligands around the central metal atom
  - Cis-trans
    - occurs when two distinct ligands are located at 180 or 90 degrees from each other
      - Square planar or octahedral only
  - Meridional-facial
    - Occurs when three distinct ligands are located around an octahedral complex
    - Mer - if ligands are mutually planar in the octahedral complex
    - Fac - if they define one face of the octahedron

Meridional-Facial

15
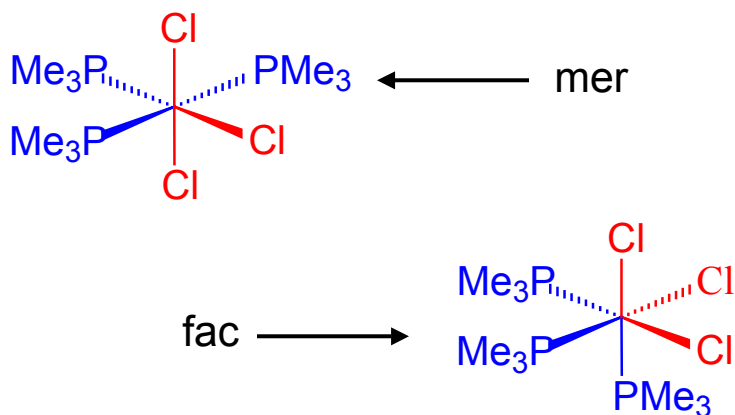
Optical Isomerism

- Transition metal complexes can also exhibit optical isomerism
  - That is defined as formation of relatively stable pairs of complexes that are not superimposable on their mirror images
- Absolute configuration is designated as lambda (Λ) or delta (Δ)
  - Arrange the species as
  - Δ - right handed screw axis
  - Λ - left handed screw axis

$[Co(en)_3]^{3+}$

Δ

Λ
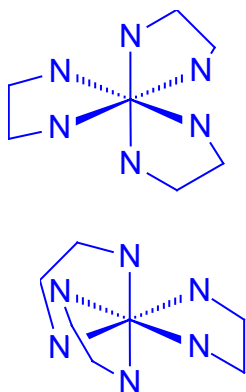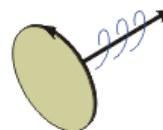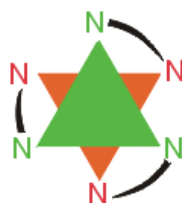
Δ-$[Co(en)_3]^{3+}$

Λ-$[Co(en)_3]^{3+}$

Sigma and Pi Ligands

- Just as in covalent bonding main group chemistry, sigma bonds form first
- Much of the interesting stability and chemistry comes from pi bonding

- Recall:
  - Sigma bonds = electron density build up along the internuclear axis
  - Pi bonds = nodal plane for the electron density along the internuclear axis

Sigma Bonding Ligands

- All ligands so far have been using sigma bonding
  - donate electrons from lone pairs to the metal center typically from either *s* or *p* orbitals
  - typical examples amines, water, nitrite ion, alkyl ligands

- all pi bonding ligands are also sigma bonding species
 - form sigma bonds first, why?

Pi Bonding Ligands

- Ligands capable of forming pi bonds with the metal. There are two types:
  - Pi bases (*e.g.* halogens particularly Cl⁻, I⁻, Br⁻)
    - Donating electron density to the metal atom
    - Similar to sigma bonding
    - Requires low energy filled pi type orbitals on L
  - Pi acids (*e.g.* CO)
    - Accepting electron density from the metal atom
    - "reverse" bonding, also known as back bonding
    - Requires empty pi type orbitals on L

Pi Bonding Ligands

- CO – carbonyls are very important pi acid, undergo pi back bonding with metal atoms
  - Have an unoccupied MO which is pi type, can accept electron density from Metal "d" orbitals.
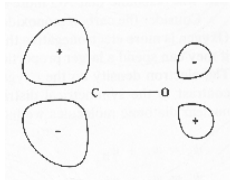
- Phosphorous Ligands: limited pi acid
- Halogen ligands: pi base
  - I⁻, Br⁻ better than F⁻,Cl⁻

Kepert Model

- VSEPR theory works well for p-block species
  - Based on lone pairs occupying space in a complex
- Would expect lone pairs to affect geometry of transition metal complexes

$$V(H_2O)_6^{3+} \quad d^2 \qquad Octahedral$$
$$Co(H_2O)_6^{3+} \quad d^6 \qquad Octahedral$$
$$Zn(H_2O)_6^{2+} \quad d^{10} \qquad Octahedral$$

Kepert Model

- Presumes that ligands geometry is not determined by the presence of lone pairs on the central atom
- Ligand-ligand repulsion determines geometry
- Ligand geometry may be constrained by other factors
  - Ligand back bone
    - Chelating ligands, tripodal ligands
  - Specific orbital overlap (d^8 *square planar systems)*

Electronic Structure of Coordination Complexes

- two models are used to describe the electronic structure of coordination complexes
  - Crystal Field Theory
  - Ligand Field Theory

- as with MO theory/VB theory both have different strengths and weaknesses
- both are obsessed (as are we) with what happens to the *d* electrons of metal atoms

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VB Theory

Uses hybridiz'n schemes including s,p,d and f orbitals to form appropriate hybrid orbitals

CN	Geometry	AO's	Hybrid
2	Linear	s, p_z	sp
3	Trig.planar	s, p_x, p_y	sp^2
4	Tetrahedral	s,p_x,p_y,p_z	sp^3
4	Sq.planar	s,p_x,p_y, d_{x2-y2}	sp^2d
5	TBP	s,p_x,p_y,p_z d_{z2}	sp^3d
5	SqPyr	s,p_x,p_y,p_z d_{x2-y2}	sp^3d
6	Octahedral	s,p_x,p_y,p_z d_{z2},d_{x2-y2}	sp^3d^2

Application of VB Theory

- Use vacant orbitals to accept electrons donated from L
- Usually *d* orbitals occupied by electrons from the central metal are left out of the hybridization
- Limitations
  - Overly simplistic
  - Requires incorporation of high energy empty d orbitals when lower d orbitals are singly occupied
  - Too localized a picture

Crystal Field Theory

- older theory
- simpler, easier to work with visually
  - similar to VB theory in that respect
- based on ionic crystal systems and therefore ignores covalent interactions between ligands and metal atoms
- basic premise .....

CF Theory Premise

- based on ionic systems so ligands are negative ions and metal centre is positive
- ligands are modeled by negative point charges arrayed around the central metal ion
- complex is held together by electrostatic attraction but .....
  - some orbitals on the metal are repelled by the point charge of L, particularly among the *d* orbitals
  - breakdown of *d* orbital degeneracy
  - leads to **LIGAND FIELD SPLITTING**
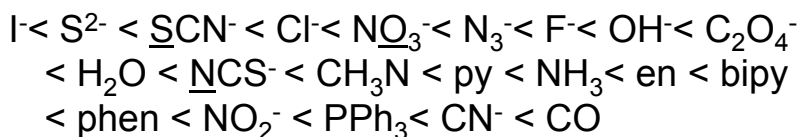
CF Theory and Octahedral Complexes
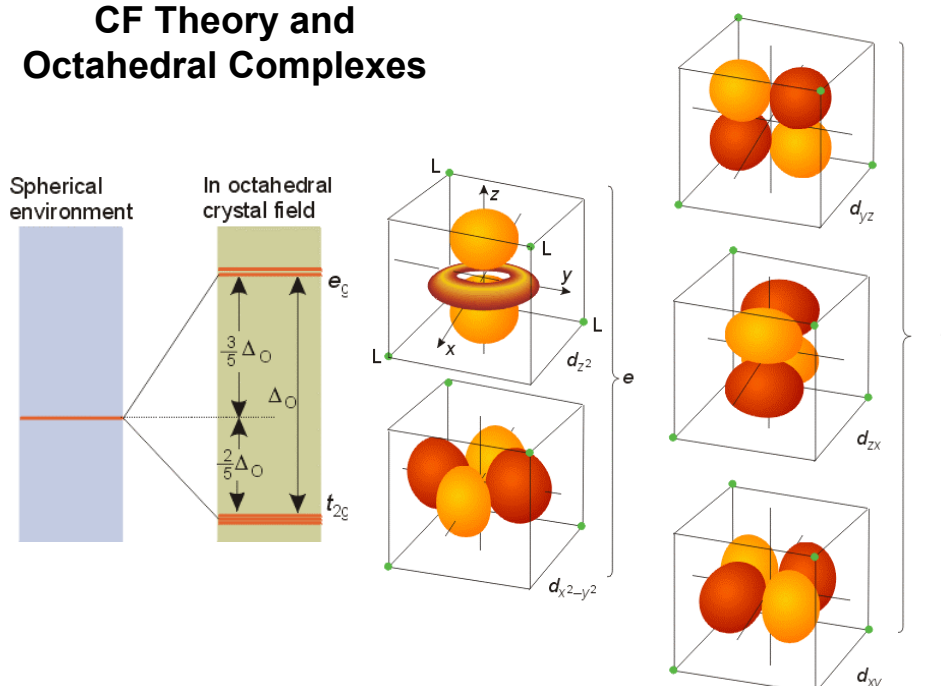
Ligand Field Splitting: Δ_o

- describes the separation between previously degenerate *d* orbitals
- very important energy level because these are typically the frontier (HOMO and LUMO)
- controls
  - visible appearance
  - magnetic properties
- most easily measured by UV-vis spectroscopy on some simple systems
  - systems with one *d* electron

Spectrochemical Series

- R. Tsuchida found that the ligands used can alter the absorption of a one electron complex
  - therefore the ligand must alter Δ_o
- proposed an ordering of ligands based on their "splitting power":

$I^- < S^{2-} < \underline{S}CN^- < Cl^- < N\underline{O}_3^- < N_3^- < F^- < OH^- < C_2O_4^-$
$< H_2O < \underline{N}CS^- < CH_3N < py < NH_3 < en < bipy$
$< phen < NO_2^- < PPh_3 < CN^- < CO$

Ligand Field Splitting and Metals

- the transition metal also impacts Δ_o
  - Δ_o increases with increasing oxidation number
  - Δ_o increases as you move down a group
    - (i.e. with increasing principal quantum number n)
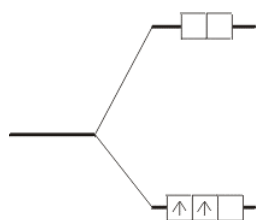
Ligand Field Stabilization Energies

- LFSE is a function of Δ_o
- weighted average of the splitting due to the fact that they are split into groups of 3 (t_{2g}) and 2 (e_g)
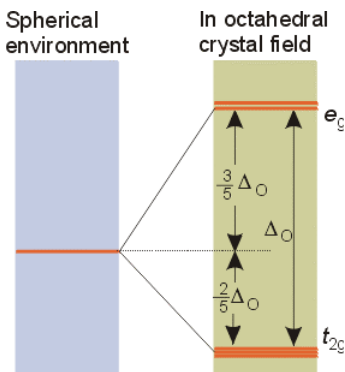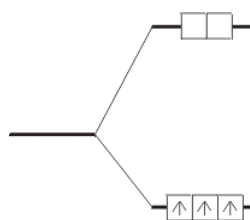
Weak Field vs. Strong Field

- now that d orbitals are not degenerate how do we know what an electronic ground state for a d metal complex is?
- need to determine the relative energies of pairing vs. Δ_o
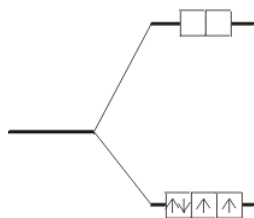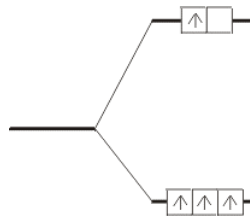

42 d^2

43 d^3

Splitting vs. Pairing

44 Strong-field d^4

45 Weak-field d^4

- when you have more than 3 but fewer than 8 *d* electrons you need to think about the relative merits pairing vs. Δ_o
- high-spin complex – one with maximum number of unpaired electrons
- low-spin complex – one with fewer unpaired electrons

Rules of Thumb for Splitting vs Pairing

- depends on both the metal and the ligands
- high-spin complexes occur when Δ_o is small
  - Δ_o is small when:
    - n is small (3 rather than 4 or 5)
      - high spin only really for 3d metals
    - oxidation state is low
      - i.e. for oxidation state of zero or 2+
    - ligands is low in spectrochemical series
      - eg halogens

Four Coordinate Complexes: Tetrahedral

- Same approach but different set of orbitals with different ligand field
- Arrangement of tetrahedral field of point charges results in splitting of energy where d_{xy}, d_{zx}, d_{yz} are repelled more by T_d field of negative charges
- So the still have a split of the d orbitals into triply degenerate (t_2) and double degenerate (e) pair but now e is lower energy and t_2 is higher.
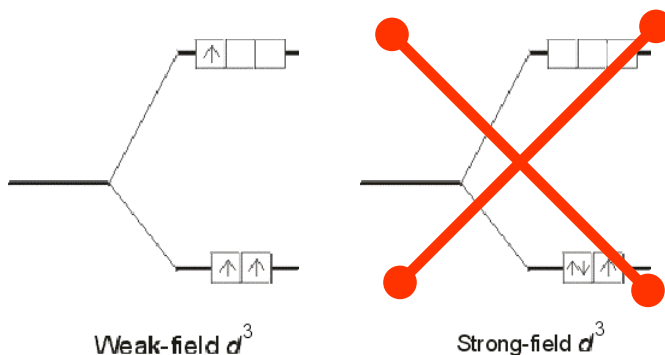
Tetrahedral Crystal Field Splitting
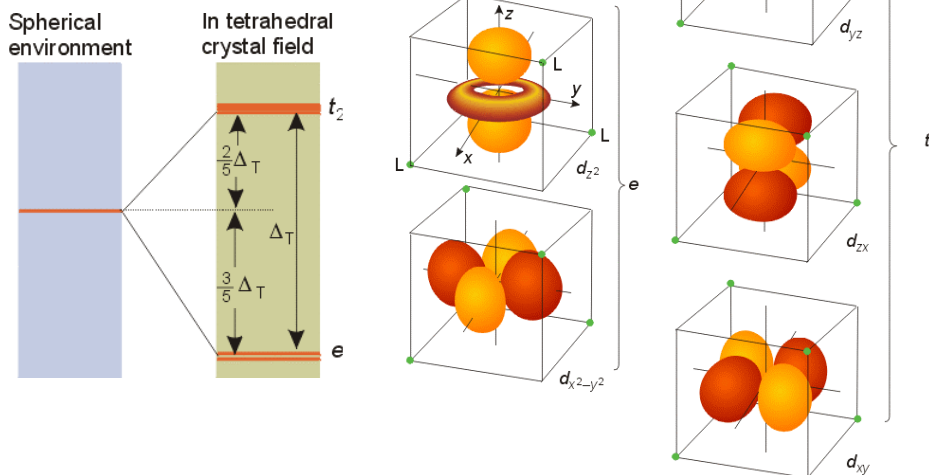
Ligand Field Splitting: Δ_T

- describes the separation between previously degenerate *d* orbitals

- Same idea as Δ_o but
- $\Delta_T < 0.5\ \Delta_o$ for comparable systems
- So …

T_d: Almost Exclusively Weak Field

- Since Δ_T is very small, we only need to consider weak field systems
  - *i.e.* high spin systems

Weak-field d^3 Strong-field d^3

Tetragonal Complexes

- Start with octahedral geometry and follow the energy as you tetragonally distort the octahedron
- Tetragonal distortion: extension along z and compression on x and y
- Orbitals with xy components increase in energy, z components decrease in energy
- Results in further breakdown of degeneracy
  - *t_{2g} set of orbitals* into $d_{yz,\,xz}$ and d_{xy}
  - *e_g set of orbitals* into d_{z2} and d_{x2-y2}

Tetragonal Orbital Energy Levels
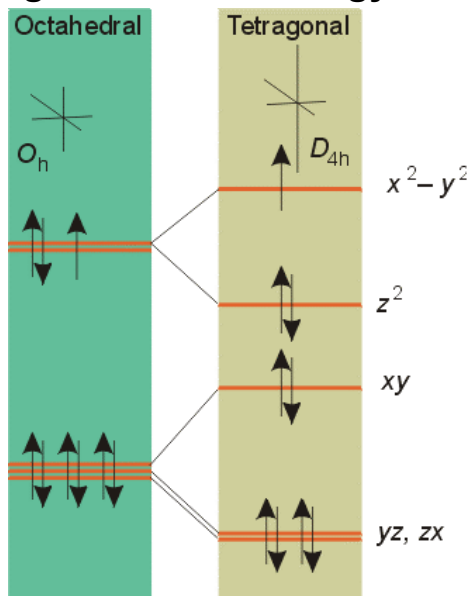
Square Planar Complexes

- extreme form of tetragonal distortion
- Ligand repulsion is completely removed from z axis
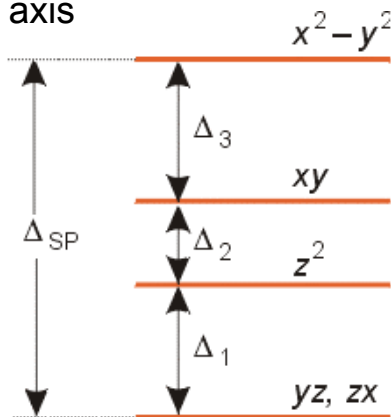
Common for $4d^8$ and $5d^8$ complexes:

Rh(I), Ir(I)

Pt(II), Pd(II)

Jahn Teller Distortion

- geometric distortion may occur in systems based on their electronic degeneracy
- This is called the Jahn Teller Effect:
- *If the ground electronic configuration of a nonlinear complex is orbitally degenerate, the complex will distort to remove the degeneracy and lower its energy*.

Jahn Teller Distortions

- Orbital degeneracy: for octahedral geometry these are:
  - $t_{2g}^3 e_g^1$ *e*g. Cr(II), Mn(III)   High spin complexes
  - $t_{2g}^6 e_g^1$ eg. Co(II), Ni(II)
  - $t_{2g}^6 e_g^3$ eg. Cu(II)
- basically, when the electron has a choice between one of the two degenerate e_g orbitals, the geometry will distort to lower the energy of the orbital that is occupied.
  - result is some form of tetragonal distortion

Ligand Field Theory

- Crystal field theory: simple ionic model, does not accurately describe why the orbitals are raised or lowered in energy upon covalent bonding.
- LFT uses Molecular Orbital Theory to derive the ordering of orbitals within metal complexes
- Same as previous use of MO theory, build ligand group orbitals, combine them with metal atomic orbitals of matching symmetry to form MO's
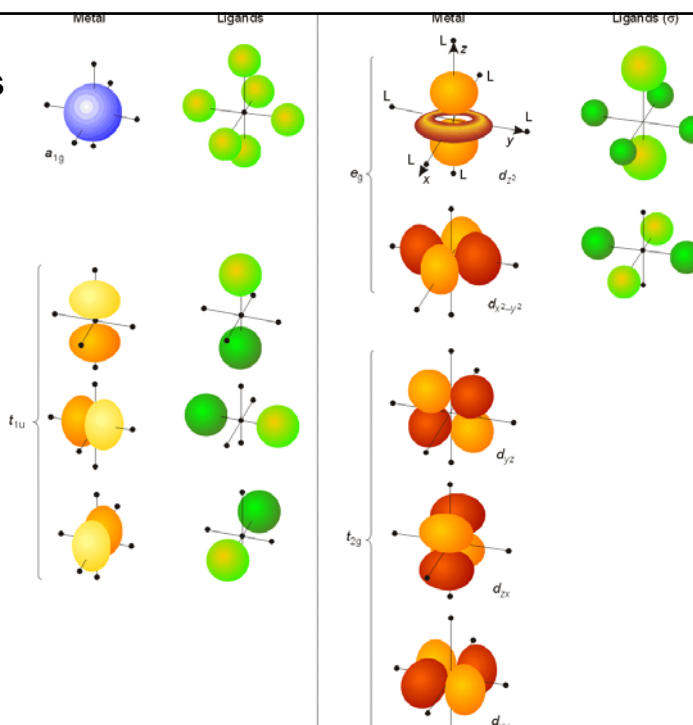
LFT for Octahedral Complexes

- Consider metal orbitals and ligand group orbitals
- Under O_h symmetry, metal atomic orbitals transform as:

Atomic Orbital	Mulliken Label	Degeneracy
s	a_{1g}	1
p_x, p_y, p_z	t_{1u}	3
d_{xy}, d_{yz}, d_{zx}	t_{2g}	3
d_{x2-y2}, d_{z2}	e_g	2

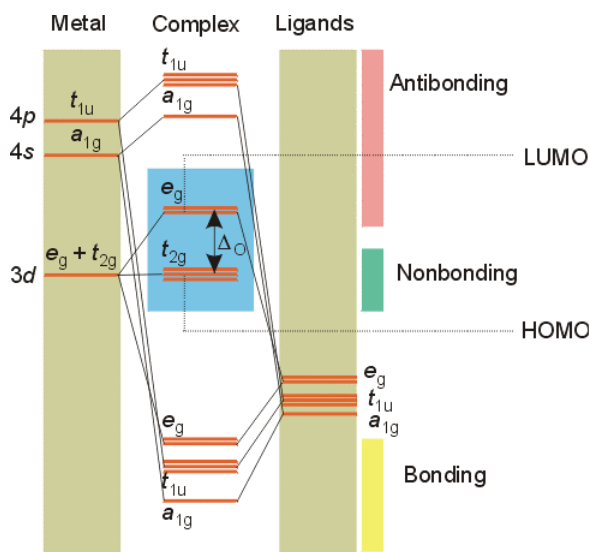## Sigma Bonding: Ligand Group Orbitals

a_{1g}

t_{1u}

e_g
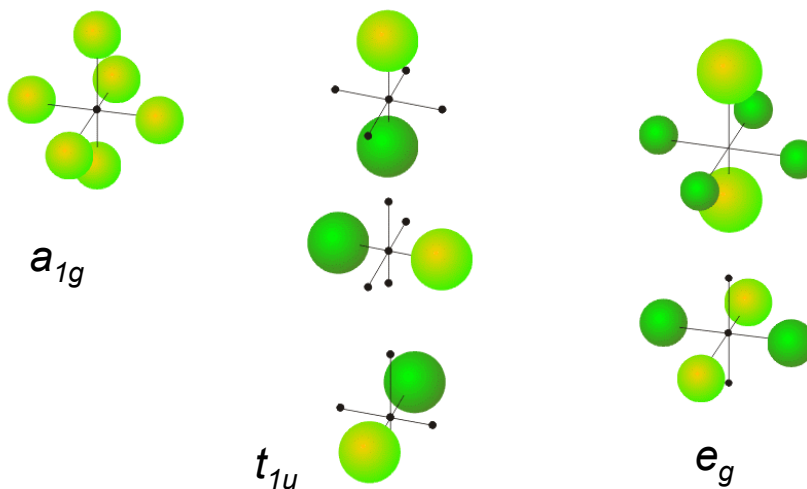
## Combinations of Metal and Ligand SALC's

Molecular Orbital Energy Level Diagram: O_h

PI Bonding

- pi interactions alter the MOELD that results from sigma bonding

- interactions occur between frontier metal orbitals and the pi orbitals of L

- two types depends on the ligand
    - pi acid - back bonding accepts e- density from M
    - pi base -additional e- density donation to the M
- type of bonding depends on relative energy level of pi orbitals on the ligand and the metal orbitals
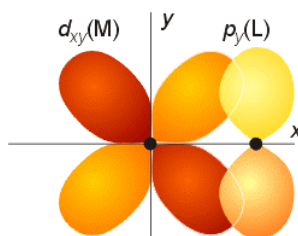
PI Bases and the MOELD: Oh

- pi base ligands contribute more electron density to the metal
- t_{2g} is split to form a bonding and antibonding pair of orbitals
- Δ_o is decreased
- halogens are good pi donors
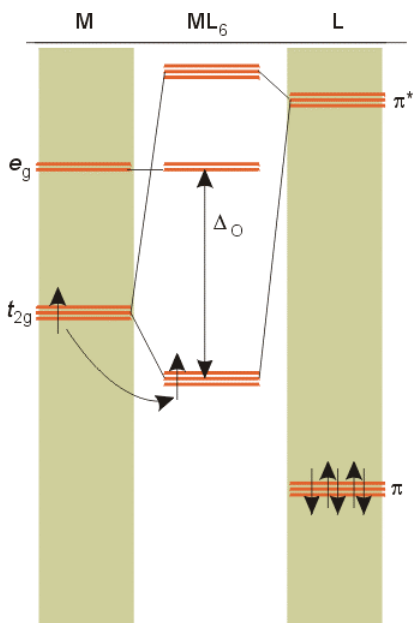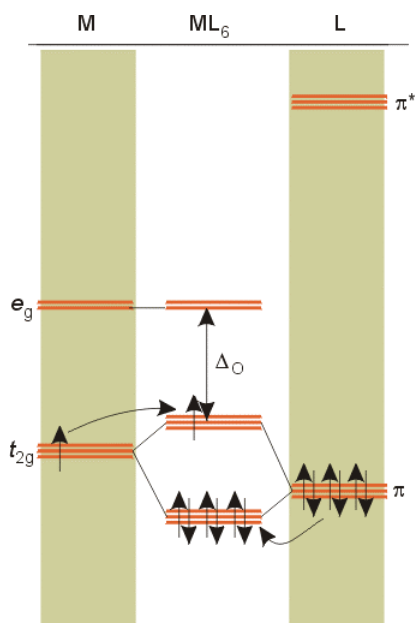
PI Acids and the MOELD: O_h

- pi acids accept electron density back from the metal
- t_{2g} is split to form a bonding and antibonding pair of orbitals
- the occupied bonding set of orbitals goes down in energy so ..
- Δ_o increases
- typical for phosphine and carbonyl ligands

Stability of Coordination Compounds

- "inert gas rule" N.V. Sidgwik, 1920's
- Transition metal form of the octet rule
- Renamed the 18 electron rule
  - Works best with octahedral low spin complexes
  - Used for determining stability of organometallic complexes particularly carbonyls

- Recognizes the particular stability of electron configurations which correspond to the noble gas atom that terminates the long period to which a metal belongs
- *i.e.* complexes want 18 electrons.

How to count to 18

- 18 electrons are derived by counting the number of valence electrons from the metal plus the number of electrons each ligand contributes
- See table 16-1 in Shriver and Atkins for complete list
- Consider all metal atoms and ligands as neutral
- Add or subtract electrons to the total to account for overall charge on the complex

Why 18 electrons?

- Look at the MOELD for O_h complexes
- 18 electrons fit where?
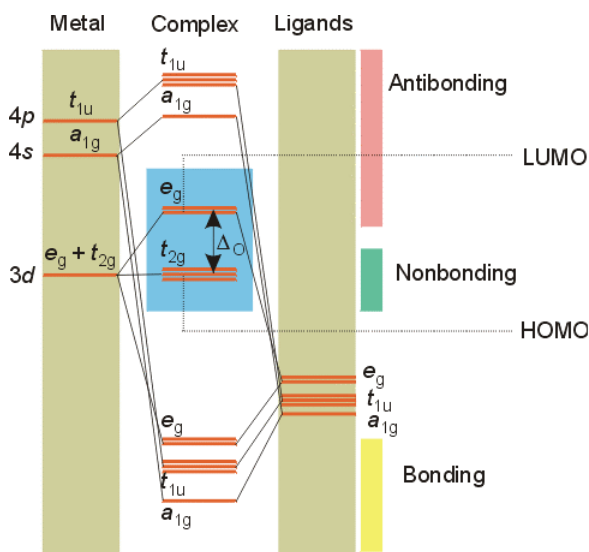
Exceptions to the 18 Electron Rule

- 16 electron complexes
  - Common on the right of the *d*- block (Co, Ni, Rh, Pd, Ir, Pt)
  - Corresponds with square planar geometries and the fact that the *d* orbitals are increasing in energy
- Other exceptions
  - Occur on the left of the *d* block
    - Low *d* number, requires lots of ligands to add up to 18
    - Steric crowding prevents the complex from reaching 18 electrons

18 Electron Rule Behaviour

Usually less than 18 electrons			Usually 18 electrons			16 or 18 electrons	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd
La	Hf	Ta	W	Re	Os	Ir	Pt
3	4	5	6	7	8	9	10

Coordination Compounds

- Lewis Acid/Base Adducts
- Definitions
  - complexes, ligands, coordination number
- Coordination Number and Shapes
- Ligands
  - Isomerism
    - linkage, geometric, optical
  - Sigma and pi bonding
- MO Theory and Crystal Field Theory
- MO Theory and Ligand Field Theory