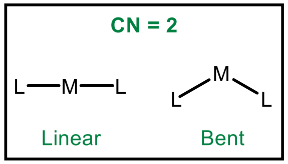
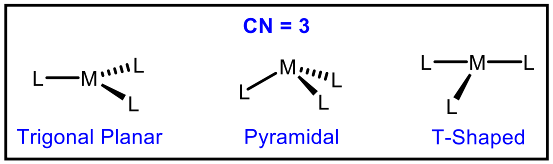
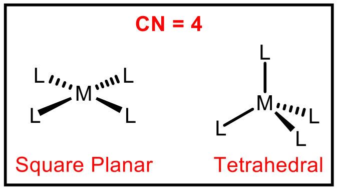
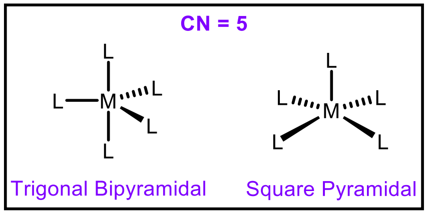
VSEPR Theory: Molecular Geometries

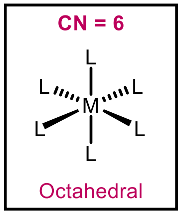
CN	Possible Geometries	Examples
2	Linear	$[Au(CN)_2]^-$, $[CuCl_2]^-$
	Bent	$SnCl_2$
3	Trigonal Planar	$[HgI_3]^-$, $[AgCl_3]^{2-}$
	Pyramidal	Specialized Systems
	T-Shaped	Specialized Systems
4	Square Planar	$RhCl(PPh_3)_3$
	Tetrahedral	$Pd(PPh_3)_4$, $TiCl_4$
5	Trigonal Bipyramidal	$Fe(CO)_5$
	Square Pyramidal	$VO(acac)_2$
6	Octahedral	Werner Complexes, $Mo(CO)_6$, $[Fe(H_2O)_6]^{2+}$







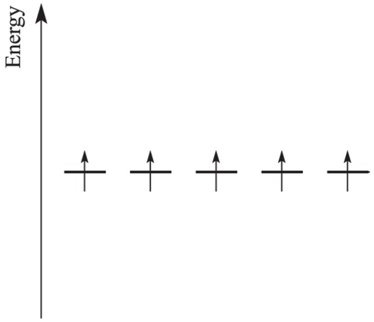




Why we need a new model?

- Coordination compounds: Unexplained Properties
  - Magnetism
  - Absorption Spectra/Colors

- Isolated metal atom
  - The five *d*-orbitals are degenerate



- Hund's rule:
  - In a set of degenerate orbitals, electrons should not be spin-paired until each orbital in the set has one electron.

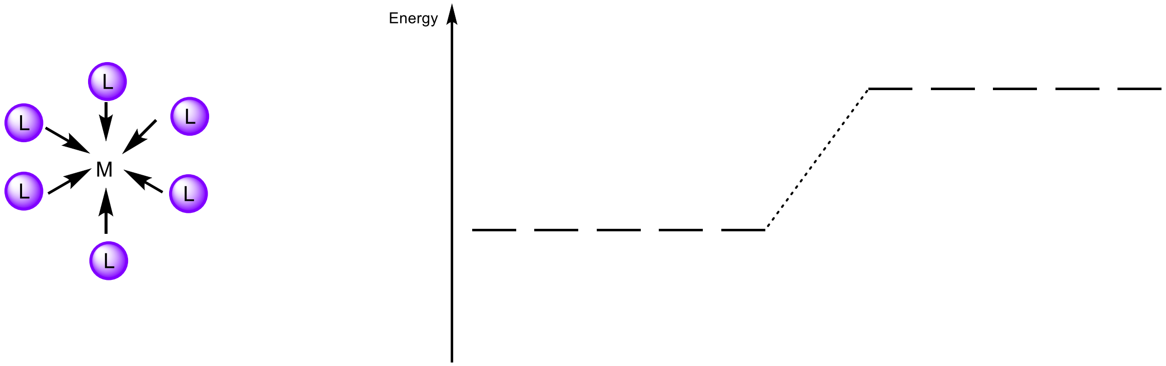
Crystal Field Theory

- **Crystal field theory** is an electrostatic bonding model where the donor ligands are thought to impart an *electric field* around the acceptor metal

- The energies of the metal *d*-orbitals are raised due to destabilization from electrostatic repulsion by this electric field (a.k.a. the "**crystal field**")

- If this crystal field were perfectly spherical, all the *d*-orbitals would be destabilized by the same amount

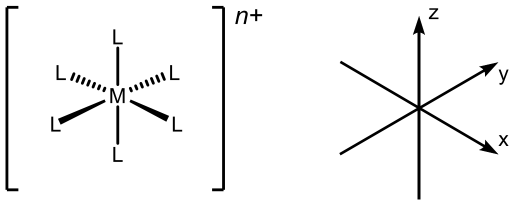
- In crystal field theory, we assume that the ligands behave like *point charges*, meaning that the crystal field is not spherical but depends on the positions of the ligands

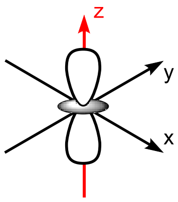


Crystal Field Theory

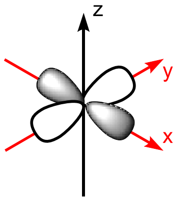
- Metal *d*-orbitals are destabilized
  - **more** if they point towards ligands and
  - **less** if they do not point towards ligands

- The Octahedral Crystal Field
  - *d*-orbitals
    - Along the cartesian axes (dz^2, dx^2-y^2)
    - In between the cartesian axes (dxy, dxz, dyz)
      - Splitting Energy(Δ_{oct})

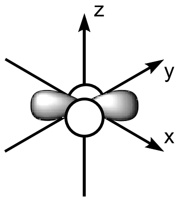




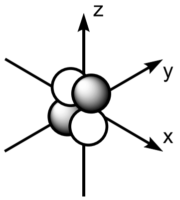
dz^2



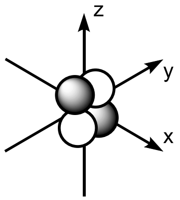
dx^2-y^2



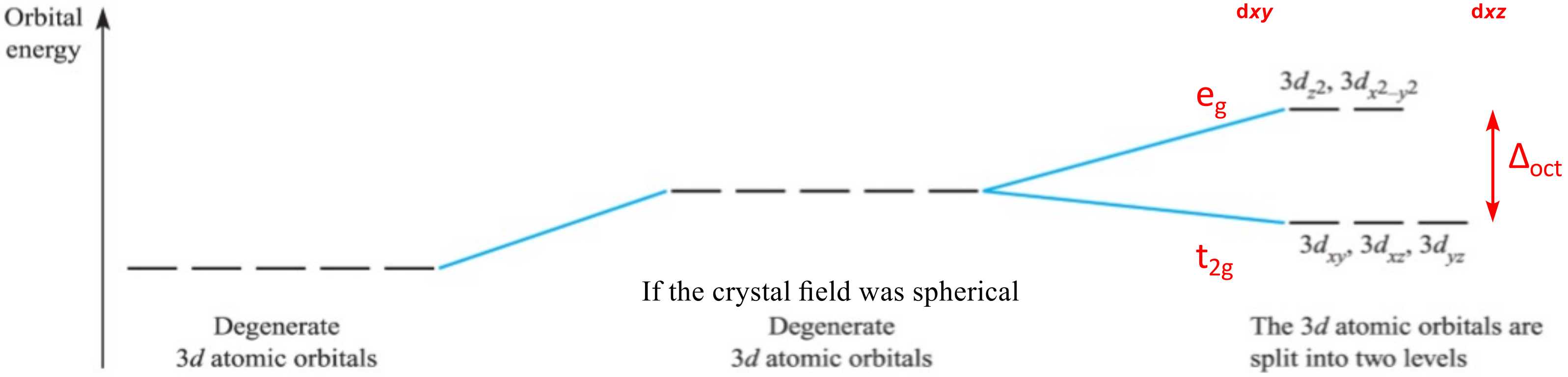
dxy



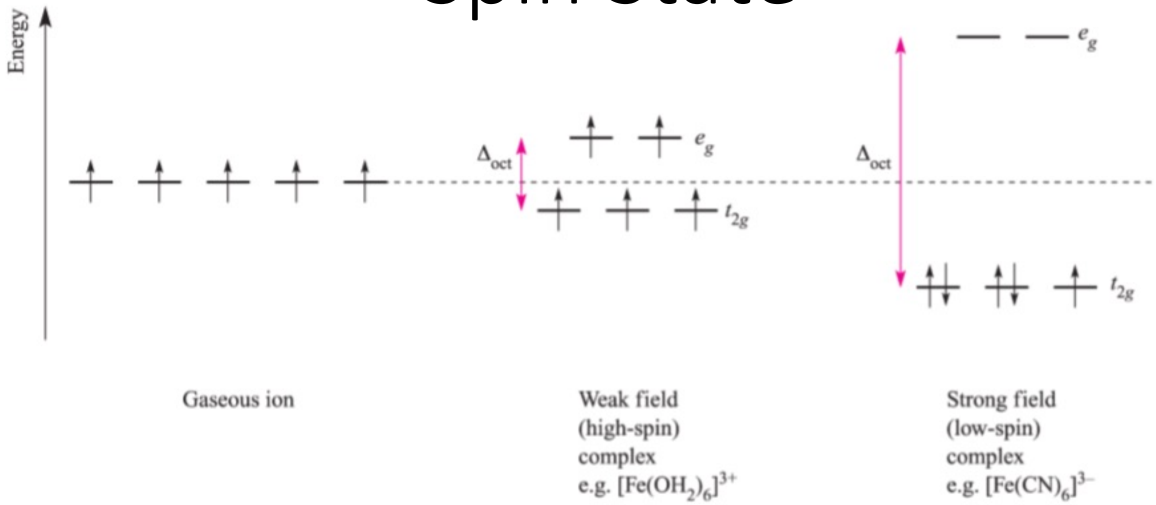
dxz



dyz

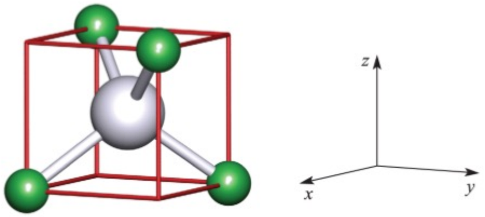


Spin State

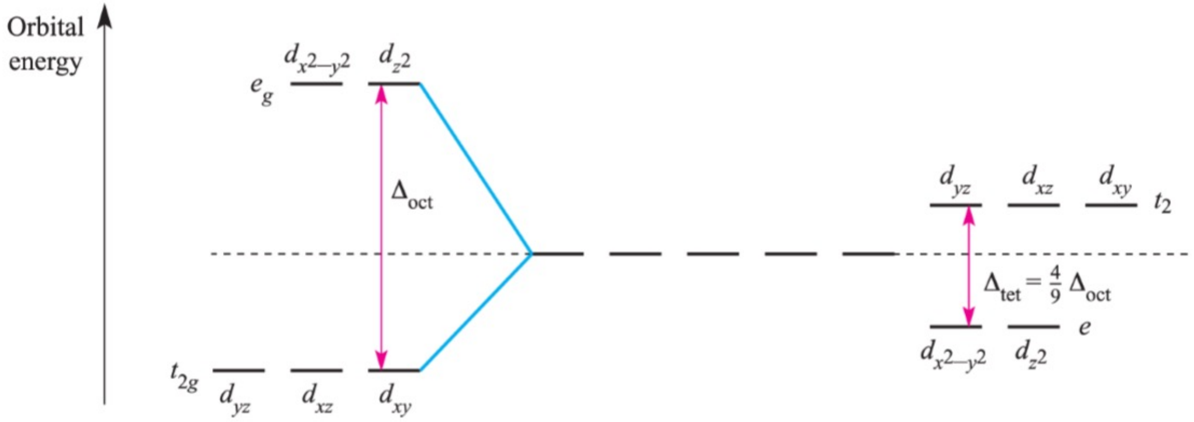


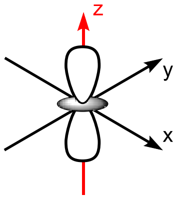
- Energetic penalty for placing two electrons in the same orbital because they repel each other. This is called **electron-pairing energy, P**.
- In a **weak field** complex, it is energetically favorable to populate the e_g level instead of pairing electrons in t_{2g}. This is because Δ_{oct} is smaller than P.
- In a **strong field** complex, it is energetically favorable to pair electrons in t_{2g} instead of populating e_g. This is because Δ_{oct} is larger than P.
- For any d^n configuration, this gives rise to two possible **spin states**, which are referred to as the **high-spin** and **low-spin** configurations based on number of unpaired electrons.
- Nature of the metal: bigger metals have better orbital overlap, which increases Δ_{oct} (3d < 4d < 5d)
  - 3d metals are often high-spin
  - 4d and 5d metals are almost always low-spin
- Magnetism:
  - Whenever two electrons are paired together in an orbital, or their total spin is 0, they are **diamagnetic** electrons. Atoms with all **diamagnetic** electrons are called **diamagnetic** atoms.
  - A **paramagnetic** electron is an unpaired electron. An atom is considered to be paramagnetic when it contains at least one paramagnetic electron.

Tetrahedral Crystal Field

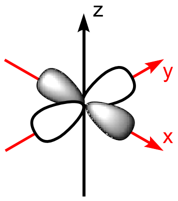


- Splitting inverted from the octahedral
- Crystal field splitting will be smaller

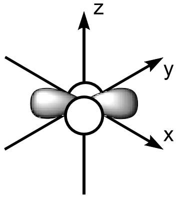




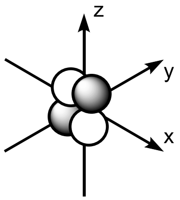
dz^2



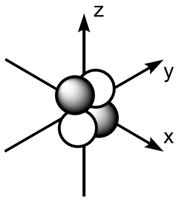
dx^2-y^2



d*xy*



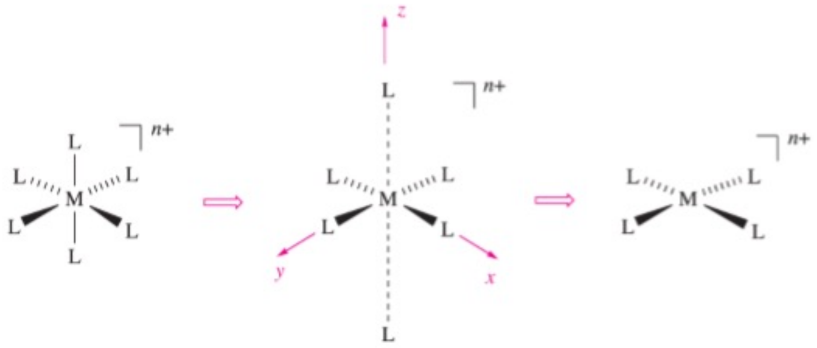
d*xz*

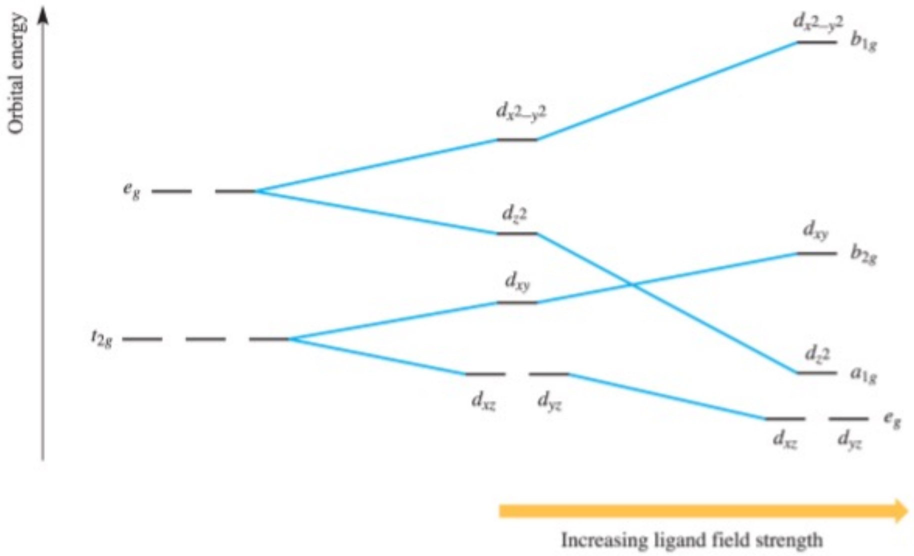


d*yz*

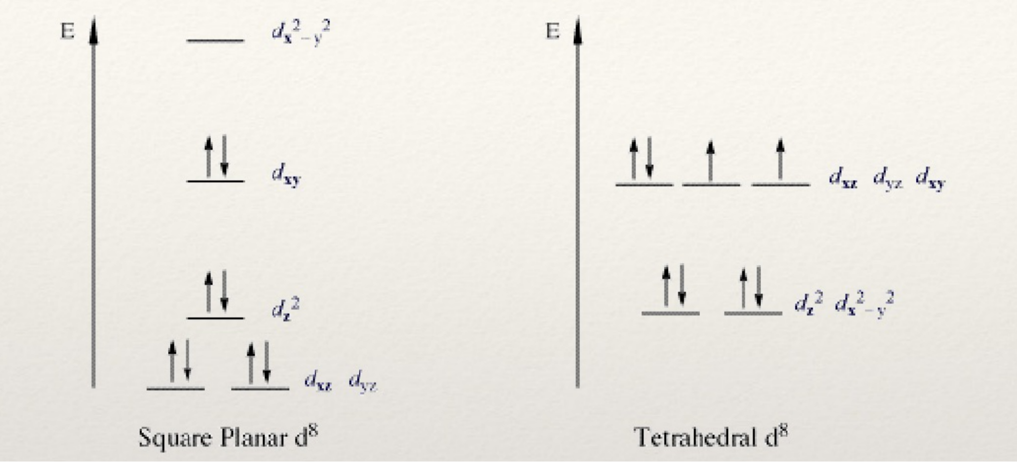
Square planer Crystal Field

- can be derived from the octahedral crystal field
- Removal of ligands along the *z*-axis decreases repulsion with the dz^2 orbital
  - stabilizing it dramatically
- The dx^2-y^2 orbital is especially destabilized
  - all 4 ligands point at it





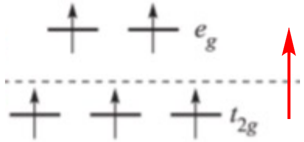
Square planer vs tetrahedral



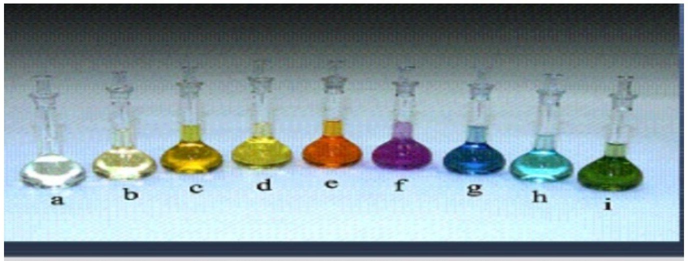
- Square planar molecules usually have d^8 configurations
- Tetrahedral d^8 molecules are **high-spin**
- square planar d^8 molecules are **low-spin**
- This is because of the large dxy-dx^2-y^2 splitting in the square planar crystal field
- **Strong field** ligands favor square planar, **weak field** ligands favor tetrahedral
- Second and third row **metals** (4d and 5d metals) with d^8 configurations are always square planar (stronger fields), while first row metals (3d metals) can be either

Factors affecting the crystal field strength

- Magnitude of the crystal field splitting (Δ)
  - Color:
    - Transitions between the t_{2g} and e_g : visible region of the EMR spectrum
    - coordination complexes are often highly colored
  - Spin state
  - Geometry



- Factors affecting the crystal field strength
  - Coordination geometry
  - Metal size & charge
  - Ligand identity



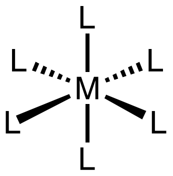
The complexes of cobalt (III) show the shift in color due to the ligand.

(a) CN^- (b) NO_2^- (c) phen (d) en (e) NH_3

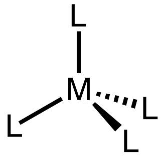
(f) gly (g) H_2O (h) ox^{2-} (i) CO_3^{2-}

Factors affecting the crystal field strength

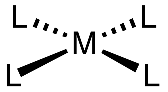
- Coordination geometry



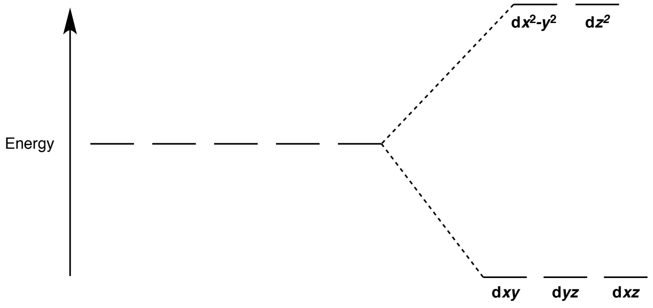
Octahedral

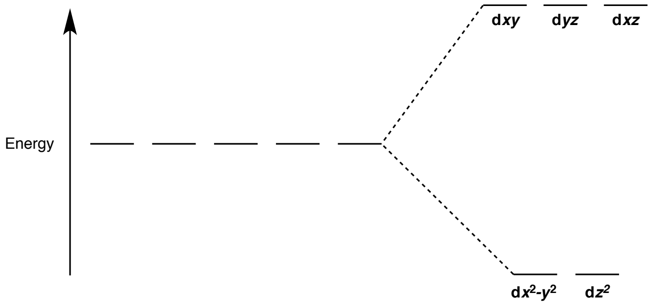


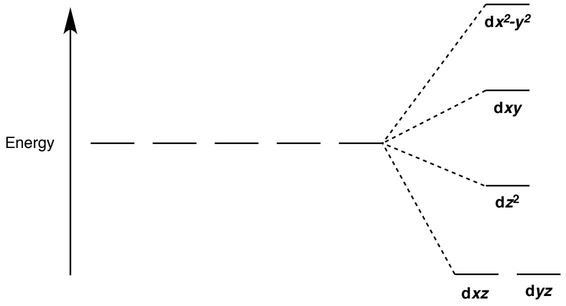
Tetrahedral



Square Planar

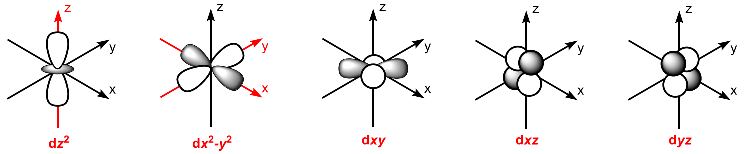




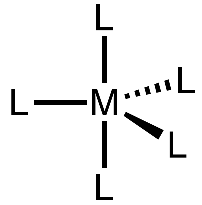


Factors affecting the crystal field strength

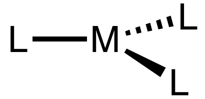
- Coordination geometry



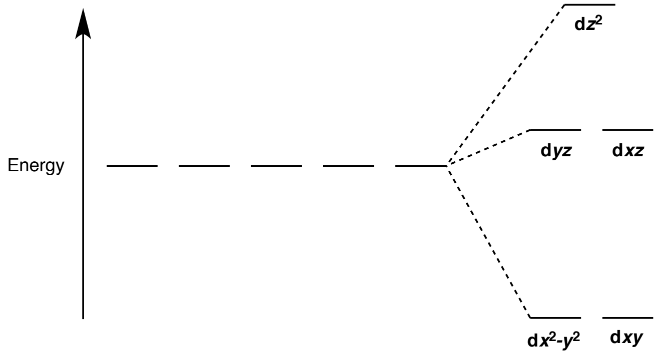
Linear

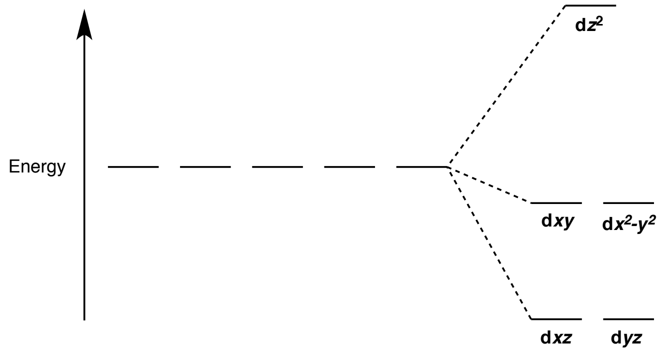


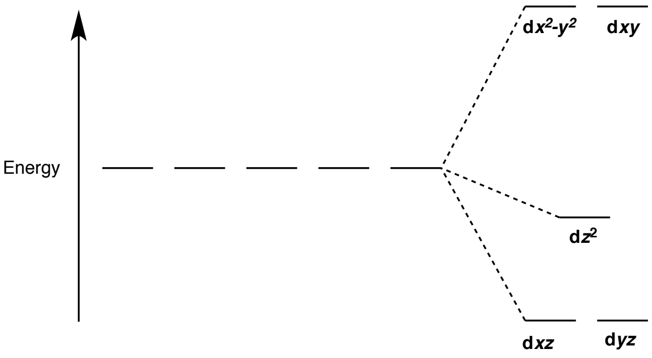
Trigonal Bipyramidal



Trigonal Planar

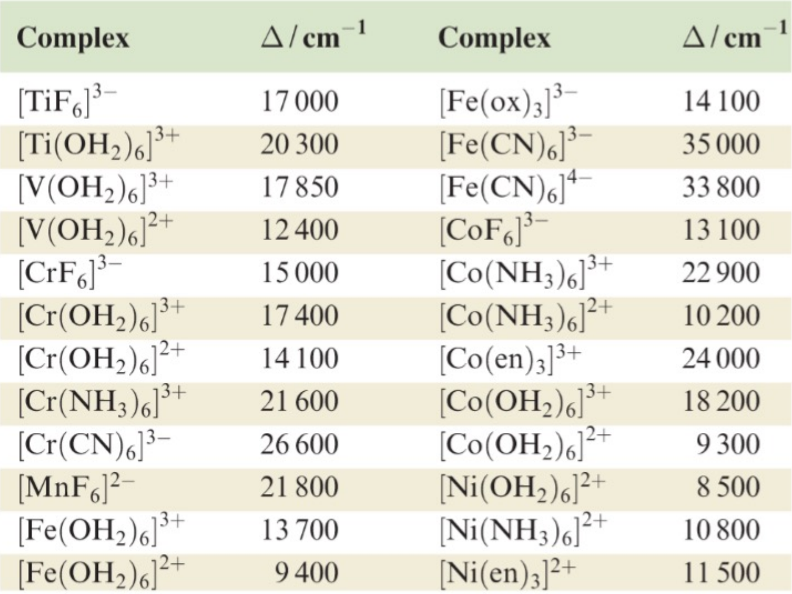






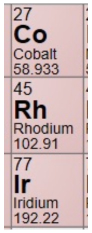
Factors affecting the crystal field strength

- Δ_{oct} obtained from UV-Vis measurements:



Complex	Δ / cm^{-1}	Complex	Δ / cm^{-1}
$[TiF_6]^{3-}$	17 000	$[Fe(ox)_3]^{3-}$	14 100
$[Ti(OH_2)_6]^{3+}$	20 300	$[Fe(CN)_6]^{3-}$	35 000
$[V(OH_2)_6]^{3+}$	17 850	$[Fe(CN)_6]^{4-}$	33 800
$[V(OH_2)_6]^{2+}$	12 400	$[CoF_6]^{3-}$	13 100
$[CrF_6]^{3-}$	15 000	$[Co(NH_3)_6]^{3+}$	22 900
$[Cr(OH_2)_6]^{3+}$	17 400	$[Co(NH_3)_6]^{2+}$	10 200
$[Cr(OH_2)_6]^{2+}$	14 100	$[Co(en)_3]^{3+}$	24 000
$[Cr(NH_3)_6]^{3+}$	21 600	$[Co(OH_2)_6]^{3+}$	18 200
$[Cr(CN)_6]^{3-}$	26 600	$[Co(OH_2)_6]^{2+}$	9 300
$[MnF_6]^{2-}$	21 800	$[Ni(OH_2)_6]^{2+}$	8 500
$[Fe(OH_2)_6]^{3+}$	13 700	$[Ni(NH_3)_6]^{2+}$	10 800
$[Fe(OH_2)_6]^{2+}$	9 400	$[Ni(en)_3]^{2+}$	11 500

- Metal size & charge
  - Metal spectrochemical series (increasing Δ_{oct}):
    - Mn(II) < Ni(II) < Co(II) < Fe(III) < Cr(III) < Co(III) < Ru(III) < Mo(III) < Rh(III) < Pd(II) < Ir(III) < Pt(IV)



27
Co
Cobalt
58.933
45
Rh
Rhodium
102.91
77
Ir
Iridium
192.22

- Ligand identity
  - Ligand spectrochemical series (increasing Δ_{oct}):
    - $I^- < Br^- < [\underline{S}CN]^- < Cl^- < F^- < [OH]^- < [ox]^{2-} = H_2O < [\underline{N}CS]^- < NH_3$ < en < bpy < phen < $[CN]^-$ = CO

π-donors σ-donors π-acceptors

HSAB Classifications

	Ligands (Lewis bases)	Metal centres (Lewis acids)
Hard; class (a)	F^-, Cl^-, H_2O, ROH, R_2O, $[OH]^-$, $[RO]^-$, $[RCO_2]^-$, $[CO_3]^{2-}$, $[NO_3]^-$, $[PO_4]^{3-}$, $[SO_4]^{2-}$, $[ClO_4]^-$, $[ox]^{2-}$, NH_3, RNH_2	Li^+, Na^+, K^+, Rb^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Sn^{2+}, Mn^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, Cr^{3+}, Fe^{3+}, Co^{3+}, Y^{3+}, Th^{4+}, Pu^{4+}, Ti^{4+}, Zr^{4+}, $[VO]^{2+}$, $[VO_2]^+$
Soft; class (b)	I^-, H^-, R^-, $[CN]^-$ (*C*-bound), CO (*C*-bound), RNC, RSH, R_2S, $[RS]^-$, $[SCN]^-$ (*S*-bound), R_3P, R_3As, R_3Sb, alkenes, arenes	Zero oxidation state metal centres, Tl^+, Cu^+, Ag^+, Au^+, $[Hg_2]^{2+}$, Hg^{2+}, Cd^{2+}, Pd^{2+}, Pt^{2+}, Tl^{3+}
Intermediate	Br^-, $[N_3]^-$, py, $[SCN]^-$ (*N*-bound), $ArNH_2$, $[NO_2]^-$, $[SO_3]^{2-}$	Pb^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Os^{2+}, Ru^{3+}, Rh^{3+}, Ir^{3+}

- **Hard-soft acid-base principle**: Hard acids form more stable complexes with hard bases, while soft acids prefer to bind soft bases.
  - **Hard** ions :
    - small, densely charged, and non-polarizable.
    - resemble point charges.
  - **Soft** ions :
    - large, diffusely charged, and highly polarizable
    - resemble mushy, smeared electron clouds.