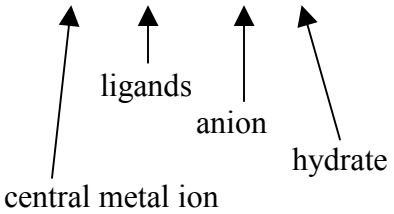
Chapter 24
Chemistry of Coordination Compounds

- Transition metal compounds (demo samples)
  - variable oxidation number
  - colored
  - unusual composition
  - often contain covalent compounds bonded to the metal
    - hydrates
  - Lewis acid–base adduct
  - coordinate covalent bonds
  - unusual magnetic properties

24.1 The Structure of Complexes

- Contain coordinate covalent bonds
- Unusual composition: Central metal ion or atom + ligands + counter ion (if needed)
- Called complex ion if charged
- $[Cu(NH_3)_4]SO_4 \cdot H_2O$



Coordination Compounds

- Complex ion: $[Cu(NH_3)_4]^{2+}$
- Coordination compound: K_2CuCl_4
- Complex ion: $[CuCl_4]^{2-}$
- Examples in nature:
  - heme
  - chlorophyll
  - enzymes
- Industrial catalysts; agents in electroplating baths; extraction of metals from ores

$CoCl_3 \cdot nNH_3$

- Consider $CoCl_3 \cdot nNH_3$, with n = 4, 5, 6
- How can we have compounds with these various compositions?
- Dissolve in water and add $AgNO_3$. Some Cl^- precipitates as AgCl immediately, some much more slowly. This indicates the relative number of Cl^- that are ionic or covalent.
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Composition	Color	No. Cl^- pptd	Formula
$CoCl_3 \cdot 6NH_3$	yellow	3	$[Co(NH_3)_6]Cl_3$
$CoCl_3 \cdot 5NH_3$	purple	2	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3 \cdot 4NH_3$	green	1	$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3 \cdot 4NH_3$	violet	1	$[Co(NH_3)_4Cl_2]Cl$

- The green and violet compounds must have some further difference.

- All have 6 ligands (coordination number = 6)

$CrCl_3 \cdot 6H_2O$

- Contains primarily $Cr(H_2O)_4Cl_2^+$
- On standing in solution, gives a mixture of:
  - $Cr(H_2O)_4Cl_2^+$ (light green)
  - $Cr(H_2O)_5Cl^{2+}$ (dark green)
  - $Cr(H_2O)_6^{3+}$ (blue–gray)
- Can measure the ion charge by the behavior on an ion exchange column.
- The mixture separates into colored bands on the column.

Coordination Sphere

- Nature of coordination compounds is determined by both the oxidation number of the central ion and its coordination number.
- The coordination number is (mostly) constant for a metal with a given oxidation number.
- First coordination sphere: central metal ion and its ligands

First Coordination Sphere

- Coordination number is often 2 x oxidation number (many exceptions)
- Mostly predictable geometry:
  Coordination number = 2, linear
  Coordination number = 4, square planar or tetrahedral
  Coordination number = 6, octahedral

Ligands

- Molecules or anions (rarely cations)
- Molecules are given the molecular name, but H_2O is aqua and NH_3 is ammine.
- Anions are named with the anion name, but with an ending of –o

Formula and Names of Some Ligands

H_2O	aqua	NH_3	ammine
CO	carbonyl	NO	nitrosyl
OH^-	hydroxo	O^{2-}	oxo
F^-	fluoro	Cl^-	chloro
Br^-	bromo	I^-	iodo
$–CN^-$	cyano	$–NC^-$	isocyano
$–NCS^-$	isothiocyanato	$–SCN^-$	thiocyanato
SO_4^{2-}	sulfato	NO_3^-	nitrato
$–NO_2^-$	nitro	$–ONO^-$	nitrito
CO_3^{2-}	carbonato		
$H_2NCH_2CH_2NH_2$	ethylenediamine		

Reactions of Coordination Compounds

- How can we prepare coordination compounds or change them into other compounds?

Redox Reactions

- Two possible mechanisms:
  - Outer sphere — coordination spheres remain intact
  - Inner sphere — ligand transfer between coordination spheres

Outer Sphere

- $[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \rightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}$
- The coordination spheres stay the same around each metal; reaction involves only transfer of an electron.

Inner Sphere

- $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_2O \rightarrow [Cr(H_2O)_5Cl]^{2+} + [Co(H_2O)_6]^{2+} + 5NH_3$
- Cl^- is transferred from Co to Cr
- $[Cr(H_2O)_5NC]^{2+}$ was prepared this way:

$[Co(NH_3)_5CN]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_2O$ –fast–> $[Cr(H_2O)_5NC]^{2+} + [Co(H_2O)_6]^{2+} + 5NH_3$

- $[Cr(H_2O)_5NC]^{2+}$ –30 sec–> $[Cr(H_2O)_5CN]^{2+}$

Substitution Reactions

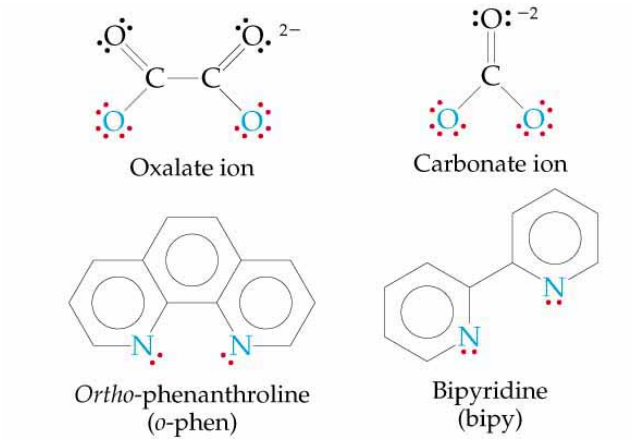
- Replace one ligand with another
- Solid state reactions can be accomplished by heating
- $[Co(NH_3)_5(H_2O)]Cl_3 \rightarrow [Co(NH_3)_5Cl]Cl_2 + H_2O$
- In solution, we can replace one ligand by another (aquation or anation or direct substitution)

$[Co(NH_3)_5Cl]^{2+} + H_2O \rightarrow [Co(NH_3)_5(H_2O)]^{3+} + Cl^-$	aquation
$[Co(NH_3)_5(H_2O)]^{3+} + NCS^- \rightarrow [Co(NH_3)_5NCS]^{2+} + H_2O$	anation
$[PtCl_4]^{2-} + NH_3 \rightarrow [PtCl_3NH_3]^- + Cl^-$	direct substitution

24.2 Chelates

- Monodentate: attached at only one atom
- Polydentate: attached at two or more separated atoms
- ethylenediamine (en): $NH_2CH_2CH_2NH_2$ attaches at the two nitrogen atoms
- ethylenediaminetetraacetic acid (EDTA): $(HOOCCH_2)_2NCH_2CH_2N(CH_2COOH)_2$ attaches at up to six positions
- called a chelate

Chelating Ligands



Chelate Effect

- Chelating ligands give much larger values of formation constants

$[Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$ $K_f = 4 \times 10^8$

$[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$ $K_f = 2 \times 10^{18}$

- Sequestering agents are chelating agents that are used to remove unwanted metal ions.
- In medicine sequestering agents are used to selectively remove toxic metal ions (e.g. Hg^{2+} and Pb^{2+}) while leaving biologically important metals.
- ($EDTA^{4-}$).

Chelating Ligands

- One very important chelating agent is ethylenediaminetetraacetate EDTA is used
  - to tie up Ca^{2+} in bathroom cleaners, shower sprays
  - to prevent blood clots
  - to remove heavy metals from the body when poisoned
  - to solubilize iron in plant fertilizer
  - to remove the iron taste from mayonnaise (arising from its preparation in iron vats)

Metals and Chelates in Living Systems

- The heme unit in hemoglobin involves a rigid chelating ligand. H_2O or O_2 or CO can be the 6th ligand.
- Chlorophyll, involved in photosynthesis, is a complex ion of magnesium(II) ion.

Nomenclature of Coordination Compounds

- Nomenclature follows different rules than for normal inorganic compounds
- Name the cation and the anion separately
- Follow the same rules for coordination compounds and complex ions.

Rules for Nomenclature

1. Name the cation, then the anion.
2. Nonionic compounds are given a one–word name.
3. Name ligands:
   a. ligands are named first and central atom last
   b. ligands are named in alphabetical order
   c. neutral ligands are named the same as the molecule (except aqua and ammine)
   d. anionic ligands are named by adding –o to the stem of the name (chloride becomes chloro)
   e. the ligand name is preceded by a Latin or Greek prefix to indicate how many are present
      di, tri, tetra, penta, hexa
      if one of these is part of the ligand name, use bis, tris, tetrakis, pentakis, hexakis
4. In a neutral or cationic complex, the name of the central metal is followed by its oxidation number in Roman numerals in parentheses.
5. In an anionic complex, the suffix –ate is added to the name of the central metal, followed by its oxidation number in Roman numerals in parentheses.

Nomenclature

- Apply the rules to the following compounds.
- $[Cr(H_2O)_5Cl]SO_4$ pentaaaquachlorochromium(III) sulfate
- $[Cr(H_2O)_5Cl]^{2+}$ pentaaquachlorochromium(III) ion
- $[Cr(H_2O)_4Cl_2]Cl$ tetraaquadichlorochromium(III) chloride
- $[Cr(H_2O)_4Cl_2]^+$ tetraaquadichlorochromium(III) ion
- $[Cr(NH_3)_3Cl_3]$ triamminetrichlorochromium(III)
- $K_2[PtCl_4]$ potassium tetrachloroplatinate(II)
- $[PtCl_4]^{2-}$ tetrachloroplatinate(II) ion
- $[Co(en)_2Cl_2]Cl$ dichlorobis(ethylenediamine)cobalt(III) chloride
- tetraamminecopper(II) sulfate $[Cu(NH_3)_4]SO_4$
- potassium hexacyanoferrate(II) $K_4[Fe(CN)_6]$
- hexaamminechromium(III) hexachloroiridate(III) $[Cr(NH_3)_6][IrCl_6$
- diaquabromochlorofluoroiodochromate(III) ion $[Cr(H_2O)_2BrClFI]^-$

- Group Work: Name these compounds
  - $[Co(NH_3)_4(H_2O)F]^{2+}$
  - $[Cu(en)_2]^{2+}$
  - $[Pt(NH_3)Cl_3]^-$
  - $[Cu(en)_2][PtCl_4]$

24.3 Isomerism

- Isomers – two or more forms of a compound having the same composition
- Isomers
  - Structural isomers (different bonding)
    - ionization isomer } Coordination sphere
    - hydration isomers } isomers
    - linkage isomers
  - Stereoisomers (identical bonding)
    - geometrical isomers
    - optical isomers

Structural Isomers

- Different ligands or different attachment of ligands
- Ionization Isomers – exchange ion between ligand and anion
  - $[Co(NH_3)_4ClBr]Cl$ and $[Co(NH_3)_4Cl_2]Br$
  - $[Pt(NH_3)_3Cl]NO_2$ and $[Pt(NH_3)_3NO_2]Cl$
- Group Work:
- Write the formula of an ionization isomer of $[Co(NH_3)_4(NO_2)_2]Br$.

- Hydration Isomers – exchange water as ligand and hydrate
  - $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$, and $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$
  - $[Co(NH_3)_5(H_2O)]Cl_3$ and $[Co(NH_3)_5Cl]Cl_2 \cdot H_2O$

- Group Work:
- Write the formula of a hydration isomer of $[Pt(NH_3)_4Cl_2]Cl \cdot H_2O$

- Linkage Isomers – ligands that can bond at more than one atomic site (ambidentate)
  - $:CN^-$ and $:NC^-$
    - $[Cr(H_2O)_5CN]^{2+}$ and $[Cr(H_2O)_5NC]^{2+}$
  - $:NCS^-$ and $:SCN^-$
    - $[Co(NH_3)_5NCS]^{2+}$ and $[Co(NH_3)_5SCN]^{2+}$
  - $:NO_2^-$ and $:O–N–O^-$
    - $[Pt(NH_3)_3NO_2]^+$ and $[Pt(NH_3)_3ONO]^+$
- Group Work:
- Write the formula of a linkage isomer of $[Co(NH_3)_5NCO]^{2+}$

Geometrical Isomers

- Different orientations of ligands within a given geometry
- Square planar and octahedral structures with two different ligands can have like ligands adjacent (cis) or opposite (trans) one another
  - $[Co(NH_3)_4Cl_2]^+$
  - $[Co(en)_2Cl_2]^+$

Octahedral Complexes

- trans-$[Co(NH_3)_4Cl_2]^+$
- cis-$[Co(NH_3)_4Cl_2]^+$

Square Planar Complexes

- $[Pt(NH_3)_2Cl_2]$ exists as cis and trans isomers

Tetrahedral Complexes

- Tetrahedral complexes have all positions equivalent and adjacent to all other positions, so there are no geometric isomers

Group Work

- Which of the following complex ions have geometric isomers?
- $[Cr(H_2O)_5Cl]^{2+}$
- $[Cr(H_2O)_4Cl_2]^+$
- $[Co(NH_3)_4(H_2O)F]^{2+}$
- $[PtBr_4]^{2-}$ (Pt(II) forms square planar complexes)
- $[Pt(NH_3)_4]^{2+}$
- $[Pt(NH_3)Br_3]^-$
- $[Pt(NH_3)_2Br_2]$

Optical Isomers

- Non–identical mirror images with the same geometric arrangement of ligands
- A set of two isomers are called enantiomers
- Enantiomers differ in optical properties — rotate plane–polarized light in opposite directions.

- Optical isomers are mirror images of one another that cannot be superimposed.
- Check for optical isomers by checking superpositions of mirror images (rotate to superimpose)

Group Work

- Which of these have optical isomers?
  - cis –$[Co(NH_3)_4Cl_2]^+$
  - trans–$[Co(NH_3)_4Cl_2]^+$
  - cis–$[Co(en)_2Cl_2]^+$
  - trans–$[Co(en)_2Cl_2]^+$
  - $[Co(en)Cl_4]^-$
  - $[Co(en)_3]^{2+}$
  - $[Cu(en)Cl_2]$

- Tetrahedral can have optical isomers if all four ligands are different.
- Does tetrahedral MA_2B_2 have optical isomers?

24.4 Color and Magnetism

Color

- Color of a complex depends on the metal, its oxidation state, and its ligands.
- Pale blue $[Cu(H_2O)_4]^{2+}$ can be converted into dark blue $[Cu(NH_3)_4]^{2+}$ by adding NH_3(aq).
- A partially filled set of d orbitals is usually required for a complex to be colored.
- So, d^0 metal ions are usually colorless. Exceptions: MnO_4^- and CrO_4^{2-}.
- Colored compounds absorb visible light.
- The color perceived is the sum of the light not absorbed by the complex.
- The amount of absorbed light versus wavelength is an absorption spectrum for a complex.
- For example, the absorption spectrum for $[Ti(H_2O)_6]^{3+}$ has a maximum absorption occurs at 510 nm (green and yellow).
- So, the complex transmits all light except green and yellow.
- Therefore, the complex is purple.
- Differences in color are reflected in differences in electronic spectra
- A variety of colors is observed for a given metal ion with different ligands.
- Color corresponds to wavelengths that are absorbed.

Magnetism

- Many transition metal complexes are paramagnetic (i.e. they have unpaired electrons).
- There are some interesting observations. Consider a d^6 metal ion:
- $[Co(NH_3)_6]^{3+}$ has no unpaired electrons, but $[CoF_6]^{3-}$ has four unpaired electrons per ion.
- We need to develop a bonding theory to account for both color and magnetism in transition metal complexes.

24.5 Crystal Field Theory

- Covalent Compounds
  - enough bonds to maintain electroneutrality
  - diamagnetic
  - colorless
  - noble gas electron configuration
- Coordination Compounds
  - extra bonds
  - usually paramagnetic
  - colored
  - non–noble gas electron configuration

Coordinate Covalent Bond

- How do we explain the differences? We need to consider a different approach to the bonding in coordination compounds.
- We will consider two theories:
  - valence bond theory (not in Brown, LeMay, Bursten, but recall from section 9.4)
  - crystal field theory
- Other theories have been developed:
  - ligand field theory
  - molecular orbital theory

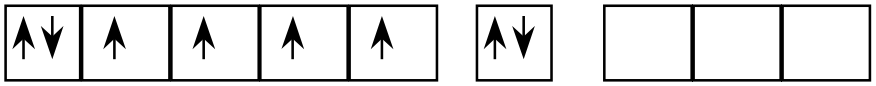
Valence Bond Theory

- Uses hybrid orbitals to hold the donated electron pairs for formation of the coordinate covalent bonds
- Can explain the structure and magnetic properties.
- Select low energy empty metal orbitals to hybridize for the appropriate geometry
- If there are not enough orbitals, pair up any unpaired metal electrons to free up orbitals.
- Hybrid orbital sets:
  - d^2sp^3 octahedral
  - sp^3 tetrahedral
  - dsp^2 square planar

Hybrid Orbitals

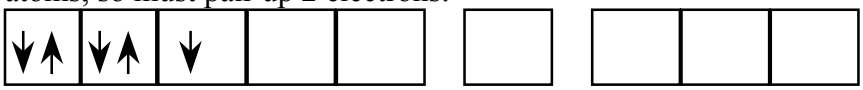
- Octahedral hybridization uses s, p_x, p_y, p_z, d_{x2-y2}, d_{z2} atomic orbitals to form six d^2sp^3 hybrid orbitals
- Consider the electron configurations.

Fe $[Ar]3d^64s^2$

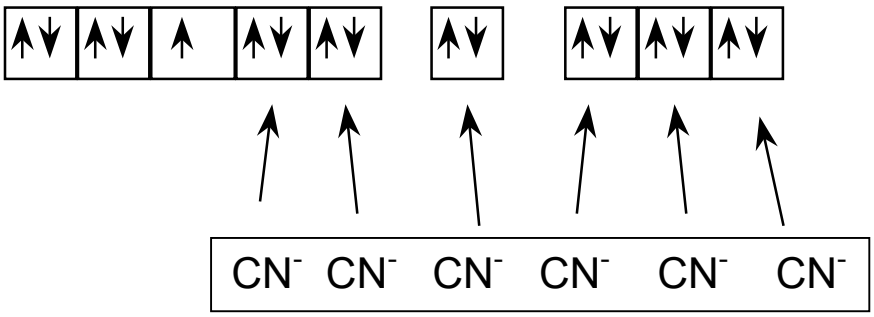


Fe^{3+} $[Ar]3d^53s^0$

- To form $[Fe(CN)_6]^{3-}$, need 6 empty orbitals to hold the electron pairs donated by the C atoms, so must pair up 2 electrons:

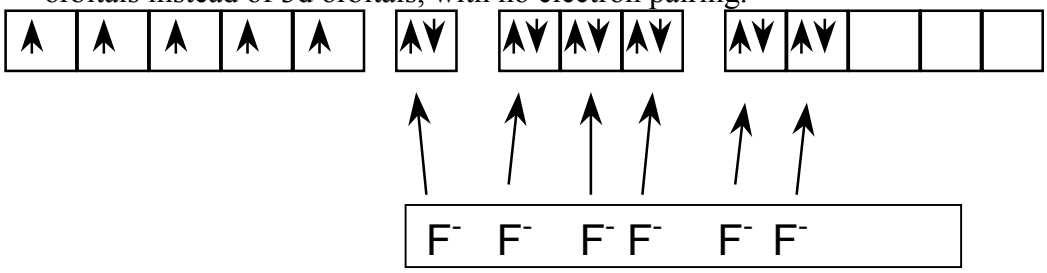


- Now we can form bonds with two d orbitals, one s orbital, and three p orbitals, giving d^2sp^3 hybridization.



Valence Bond Theory

- $[FeF_6]^{3-}$ has 5 unpaired electrons, not 1, so we have to modify this approach, using 4d orbitals instead of 3d orbitals, with no electron pairing.



Group Work

- Write box diagrams for the electron configuration of Cr(III), using high spin and low spin arrangements of 6 ligands.
- Would there be two arrangements for Cr(III)?

Group Work

- Consider the electron configurations for Co
- Co $[Ar]3d^7 4s^2$

- What is the valence bond description of $Co(NH_3)_6^{3+}$?

Valence Bond Theory

- Valence bond theory limitations:
  - explains, but does not predict
  - qualitative explanations; does not explain relative stability
  - can't explain color and spectra
  - can't explain relative stability of structural isomers

Crystal Field Theory

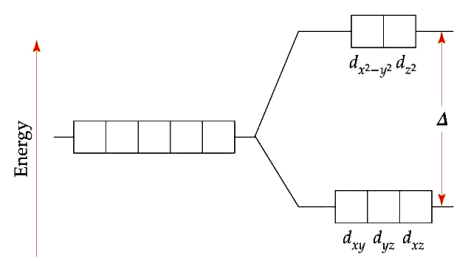
- Assumes electrostatic interactions between the metal ion and the ligands, rather than covalent bond formation
- Bonding attractions between positively charged metal ion and negatively charged electron pairs on the ligands
- Electrons on the metal (d electrons) are repelled by the ligand electrons
- Some d orbitals are repelled to a greater extent than others, which can explain magnetic properties and color
- Between Ligands
  - d_{xy}
  - d_{xz}
  - d_{yz}
- Toward Ligands
  - d_{z2}
  - d_{x2-y2}

Crystal Field Theory

- If d orbitals are placed in a spherical field, they all have the same energy.
- Note that three of the orbitals point between the axes, while two point along the axes.

Octahedral Crystal Field

- Ligands in an octahedral structure are located on the axes, so they repel the d_{x2-y2} and d_{z2} orbitals more than the others.
- Octahedral field thus splits the orbitals into two energy levels.



- The splitting of the energy levels is called Δ, the crystal field splitting energy.
- Not all d electrons have the same energy.
- It is possible to promote an electron from a lower energy orbital to a higher energy orbital, with absorption of light of a wavelength corresponding to an energy of Δ.

Tetrahedral Crystal Field

- In a tetrahedral structure, the ligands are located at opposite corners of a cube enclosing the axes.
- The orbitals are split into two energy levels, but in the reverse order of an octahedral field.
-

Orbital Occupancy in a Crystal Field

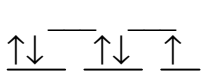
- Depends on the magnitude of Δ
- Varies with the structure
  $\Delta_{oct} > \Delta_{tetr}$ (tetra ~45% of oct)
- Varies with principal energy level
  4d > 3d (4d ~1.45 x 3d)
  5d ~ 4d (5d ~1.74 x 3d)
- Varies with charge
  3+ > 2+
- Δ varies with the metal
- Δ varies with the ligand (e.g., $CN^- > NH_3$)

Color

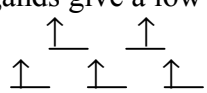
- Color arises by absorbing light and promoting an electron to a higher–energy orbital.
- For many transition metal complex ions, Δ corresponds to wavelengths of visible light, so the complexes are colored.
- We need to have partially filled d orbitals to have any electronic transitions that can give color.
- Ti(III) is violet and Ti(IV) is colorless.
- A variety of colors is observed for a given metal ion with different ligands.
- Ligands can be placed into a sequence in order of decreasing Δ
- Called the spectrochemical series
- Generally, C > N > O > F > Cl > S > Br > I
- Can predict the color, based on Δ associated with the metal, the structure, and the ligand.

Magnetism

- Whether a coordination compound is paramagnetic (attracted to a magnetic field) or diamagnetic (not attracted or repelled) can be explained by crystal field splitting.
- Strong field ligands give high Δ and electrons tend to be paired (low spin).
- $[Fe(CN)_6]^{3-}$ d^5



- Weak field ligands give a low Δ and electrons tend to be unpaired (high spin).
- $[FeF_6]^{3-}$ d^5



- Electron occupancy varies with the ligand only for the following electron configurations: d^4, d^5, d^6, d^7
- Other configurations give identical results for strong or weak field ligands.
- Tetrahedral Δ are smaller than octahedral; as a result, there are no ligands that are known

to provide a sufficiently strong field to give a low spin complex.

- All known tetrahedral complexes are high spin.
- Thus, crystal field theory can explain color and magnetism, as well as many other properties we will not discuss.